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Thesis

THE HYDROGEN BOND STRENGTH OF
TRIFLUOROACETIC ACID

by

Norman Rosenberg

(A.B., Harvard College, 1946)
submitted in partial fulfilment of the
requirements for the degree of
Master of Arts
1949

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.....Professor of Chemistry.....

I wish to acknowledge my indebtedness to Professor Lowell V. Coulter, under whom this investigation was carried out; without his constant guidance, this work would not have been possible.

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To
Mr, Pa, and Al

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Introduction and Statement of Problem.

It has long been recognized that, under certain conditions, an atom of hydrogen, already covalently bonded to one atom, is attracted by rather strong forces to a second atom, with the result that the hydrogen atom may be visualized as acting as a bond between these two atoms. This is called the hydrogen bond.

The hydrogen bond is relatively weak, being of the order of 5 kcal. per bond; it is, however, of great importance, influencing to a significant degree the physical and chemical properties of compounds of such widely separated types as water (15) and globular proteins (19).

In the past twenty years, much work has been done in an effort to elucidate the nature of the hydrogen bond. Two generalizations have been furnished by this work: first, the hydrogen bond is generally a bond through hydrogen between two atoms; second, only the most electronegative atoms are hydrogen bonded (1,11,14,19). Corollary to the second generalization, it is believed that the hydrogen bond is electrostatic in character (19), inasmuch as the hydrogen atom has only one stable bond-forming orbital (the 1s orbital) and the formation of a second bond employing a 2s orbital would lead to a highly unstable system.

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The most precise estimate of the strength of a hydrogen bond in a compound is obtained through a study of

the variation of the vapor density of the compound with temperature. This method is essentially the Dumas method for determining the molecular weight of a gas. Knowing the apparent molecular weight and the corresponding vapor pressure, it is possible to derive a relationship for the equilibrium constant for the system (polymer \rightleftharpoons monomer) and from this, the heat of association may be calculated by the van't Hoff equation. The heat of association divided by the polymerization order number yields the strength of one hydrogen bond.

An alternative method for quantitative investigation of the molecular state of the vapor of a compound is through the use of infra red absorption spectra. This method has more error associated with it.

Latimer and Rodebush (15) observed in 1920 that the dimerization of acetic acid could be explained in terms of hydrogen bond formation. This has since been shown to be a generalized phenomenon of molecules possessing a carboxyl group. In the past twenty years, numerous quantitative investigations have been made on the heats of association of several of the low molecular weight aliphatic carboxylic acids. These results are summarized in Table 1.

The dimer of formic acid has been subjected to a careful study by Pauling and Brockway (20). Using electron diffraction methods, they concluded that the structure of formic acid could best be represented as

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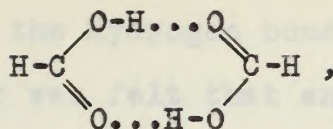
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Table 1

The Heat of Association of Some Hydrogen Bonds from Vapor Density (VD) and Spectroscopic (S) Data

Compound	Investigator	Method	$\frac{\Delta H}{\text{two bonds}}$ 14100 (ave.)*
HCOOH	Ramsperger and Porter (21)	VD	14135 *
	Coolidge (4)	VD	12400 \pm 700
	Herman (9)	S	12800 \pm 700
HCOOD	Herman (9)	S	16400 \pm 800
CH ₃ COOH	MacDougall (16)	VD	15000
	Nernst and von Wartenberg (18)	VD	13790 \pm 200
	Fenton and Garner (6)	VD	rough agreement with MacDougall
	Badger and Bauer (2)	S	14500 \pm 400
CH ₃ COOD	Ritter and Simons (23)	VD	15900 \pm 700
C ₂ H ₅ COOH	Herman and Hofstadter (10)	(most recent) S	18000 \pm 2000
C ₂ H ₅ COOD	MacDougall (16)	VD	14100 \pm 500
C ₃ H ₇ COOD	Herman and Hofstadter (10)	S	13800 \pm 700
C ₆ H ₁₃ COOH	Herman (9)	S	7050 **
	Fenton and Garner (6)	VD	

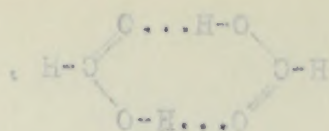
* No limits of error are assigned to these values but they are generally regarded as the product of careful work.
 **Extremely unreliable.



where the broken lines indicate hydrogen bonds. The hydrogen lies on the line joining the two oxygen atoms, and the two carboxyl groups lie in the same plane. It was believed by these authors that the highest order polymer of formic acid is the dimer. Indeed, Hammett (8) has stated that dimerization represents the full tendency toward polymerization of the carboxylic acids. However, MacDougall's work on acetic and propionic acids (16) seems to indicate that some higher order polymerization is involved in these compounds.

Ritter and Simon's work (23) confirms this viewpoint. They state that there is at least one polymer of order higher than the dimer and they have derived evidence in support of the theory that the next higher polymer is the tetramer. The evidence which these authors present seems to leave very little doubt that some polymer of order greater than two was indeed present. It is felt however that the structure suggested for the tetramer required much stronger support, inasmuch as the proposed structure involves hydrogen with a coordination number of three, which is extremely rare.

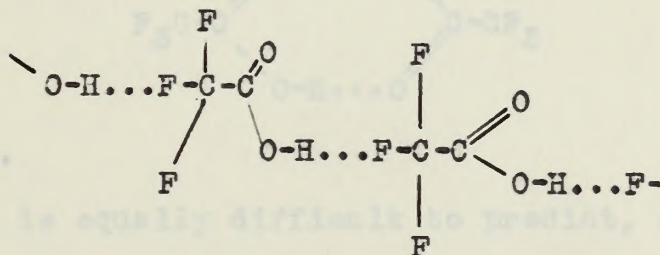
Reference to Table 1 shows that there would appear to be a gradual increase in the strength of the hydrogen bond as the substituent α to the carboxyl group becomes less electronegative. Thus, the strength of the bond for formic acid is 7.05 kcal., for acetic, 7.25 kcal., and for propionic,



where the broken lines indicate hydrogen bonds. The hydrogen lies on the line joining the two oxygen atoms, and the two carboxyl groups lie in the same plane. It was believed by these authors that the highest order polymer of formic acid is the dimer. Indeed, Hammett (8) has stated that dimerization represents the full tendency toward polymerization of the carboxylic acids. However, MacDonnell's work on acetic and propionic acids (16) seems to indicate that some higher order polymerization is involved in these compounds. Ritter and Simon's work (23) confirms this view-point. They state that there is at least one polymer of order higher than the dimer and they have derived evidence in support of the theory that the next higher polymer is the tetramer. The evidence which these authors present seems to leave very little doubt that some polymer of order greater than two was indeed present. It is felt however that the structure suggested for the tetramer required much stronger support, inasmuch as the proposed structure involves hydrogen with a coordination number of three, which is extremely rare. Reference to Table I shows that there would appear to be a gradual increase in the strength of the hydrogen bond as the substituent α to the carboxyl group becomes less electronegative. Thus, the strength of the bond for formic acid is 7.05 kcal., for acetic, 7.25 kcal., and for propionic,

9.0 kcal. Inasmuch as the hydrogen bond is primarily electrostatic in character, it was felt that an investigation of the effect of strongly electronegative substituents α to the carboxyl group would prove of interest.

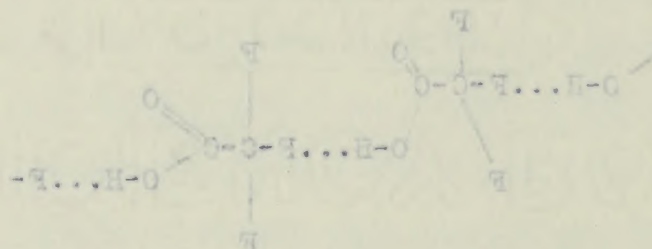
Prediction as to the effects of substituents on the strength of the hydrogen bond of the aliphatic carboxylic acids is quite complicated. It is well known that the hydrogen bond is capable of forming only between two strongly electronegative atoms. Therefore, in trifluoroacetic acid, one might visualize any of the normal $O-H...O$ bonds, and also a head-to-tail polymerization of the sort



or possibly a combination of the two. It is impossible to state with any certainty whether $O-H...O$ bonds, or $O-H...F$ bonds will predominate. As a first approximation, however, a consideration of the bond dipole moments of the $-C=O$ group and the $-C-F$ group may prove instructive. Generally, the bond moment of a carbonyl group is about 2.8 Debye units, that of a carbon-fluorine single bond, about 1.4 D. (19). (The value for the carbon-oxygen double bond is the average of a number of aliphatic ketones and, therefore, is not strictly applicable to a carboxyl group. It is felt, however, that the

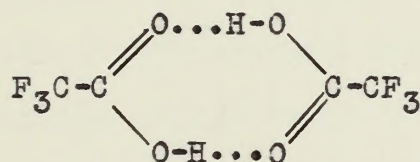
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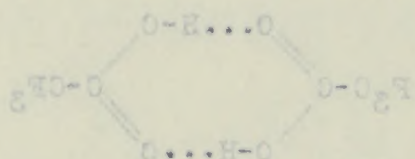
influence of the hydroxyl group does not affect the carbonyl bond moment sufficiently to detract from the qualitative cogency of the argument to follow.) Clearly, the more negative group will yield the greater coulombic interaction; therefore, one would predict that head-to-head polymerization would predominate and that head-to-tail structures would be only of the second rank in importance. Another argument in favor of O-H...O bonding is the reported electron diffraction study of trifluoroacetic acid (13) which has assigned the structure



to the dimer.

It is equally difficult to predict, even in a qualitative way, the hydrogen bond strength of trifluoroacetic acid. By consideration of the relative electronegativities of substituent groups, one would conclude that the hydrogen bond strength of trifluoroacetic acid would be less than that of acetic acid. If one assumes acetic acid as a standard of reference against which trifluoroacetic acid may be compared, the following situation is encountered. In the system as reported by Karle and Brockway, the presence of the strongly electronegative $-CF_3$ groups leads to polarization of the carboxyl groups. If one treats the hydroxyl group alone, it would appear that polarization of the hydroxyl

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oxygen will lead to a more ionic -O-H bond, and, hence, to a stronger hydrogen bond. On the other hand, polarization of the carbonyl oxygen will take place and, in all probability, to a greater extent than is the case with the hydroxyl oxygen. Since this would tend to decrease the negative charge on the oxygen to a greater extent than the positive charge on the hydrogen is increased, one is led to the conclusion that the hydrogen bond of trifluoroacetic acid will be weaker than that of acetic acid. The results of this research, however, do not confirm this prediction.

The purification apparatus consisted of two units: the fractional crystallization apparatus; and the storage system.

The fractional crystallizer is shown in Figure 3, and consisted of a pear shaped flask (A) of about 100 cc. capacity, to whose narrow end a rubber extension of about 25 cc. volume (B) was attached. A trap (H) completed the assembly. The flask was equipped with a thermocouple well (C), a stirrer (D), a stirrer support (E), an internal vacuum breakoff tip (F), a filling tube (G), a heated glass filter (I), and a stopcock (J).

oxygen will lead to a more ionic O-H bond, and, hence, to a stronger hydrogen bond. On the other hand, polarization of the carbonyl oxygen will take place and, in all probability, to a greater extent than in the case with the hydroxyl oxygen. Since this would tend to decrease the negative charge on the oxygen to a greater extent than the positive charge on the hydrogen is increased, one is led to the conclusion that the hydrogen bond of trifluoroacetic acid will be weaker than that of acetic acid. The results of this research, however, do not confirm this prediction.

Description of the Apparatus.

For purposes of description, the apparatus employed in this research may be conveniently divided into the following units: the high vacuum line; the purification apparatus; thermostat "A" (bulb thermostat); thermostat "B" (burette thermostat); bulb-and-burette assembly; electrical measuring equipment.

The high vacuum line is shown in Figure 1 and was made up of a McLeod gauge (A), a mercury diffusion pump (B), a coil heater (C), two U-type mercury valves (D,E), a cold trap (F), stopcock system (G,H), three Wolff bottles (J), and a backing pump. The line was mounted on a rack of the usual type (5,29).

The purification apparatus consisted of two units: the fractional crystallization apparatus; and the storage system.

The fractional crystallizer is shown in Figure 2, and consisted of a pear shaped flask (A) of about 100 cc. capacity, to whose narrow end a tube extension of about 25 cc. volume (B) was attached. A trap (M) completed the assembly. The flask was equipped with a thermocouple well (C), a stirrer (D), a stirrer support (E), an internal vacuum breakoff tip (F), a filling tube (G), a sintered glass filter (H), and a stopcock (J).

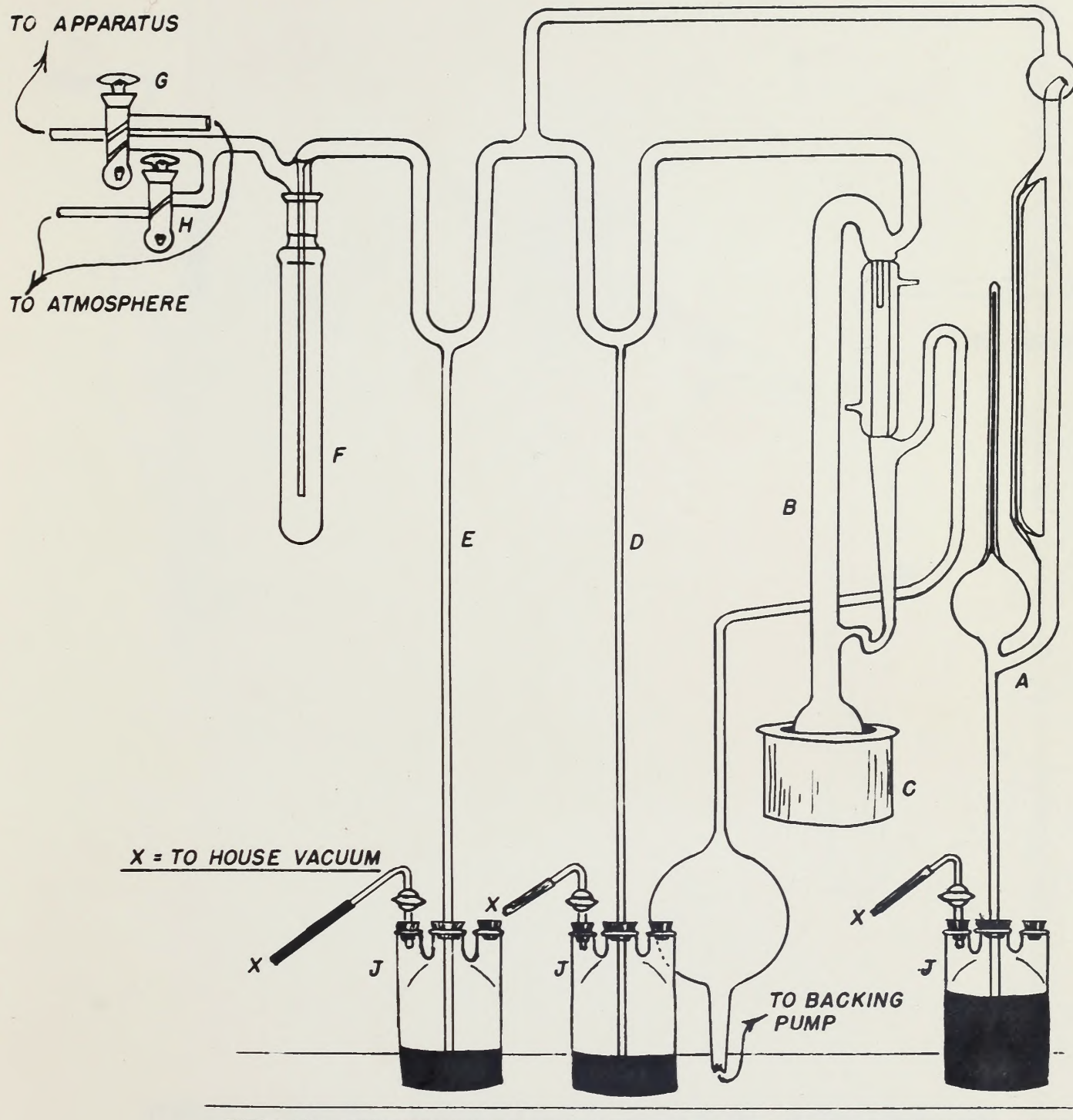
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The high vacuum line is shown in Figure 1 and was made up of a McLeod gauge (A), a mercury diffusion pump (B), a coil heater (C), two U-type mercury valves (D,E), a cold trap (F), stopcock system (G,H), three Wolff bottles (I), and a backing pump. The line was mounted on a rack of the usual type (5,29).

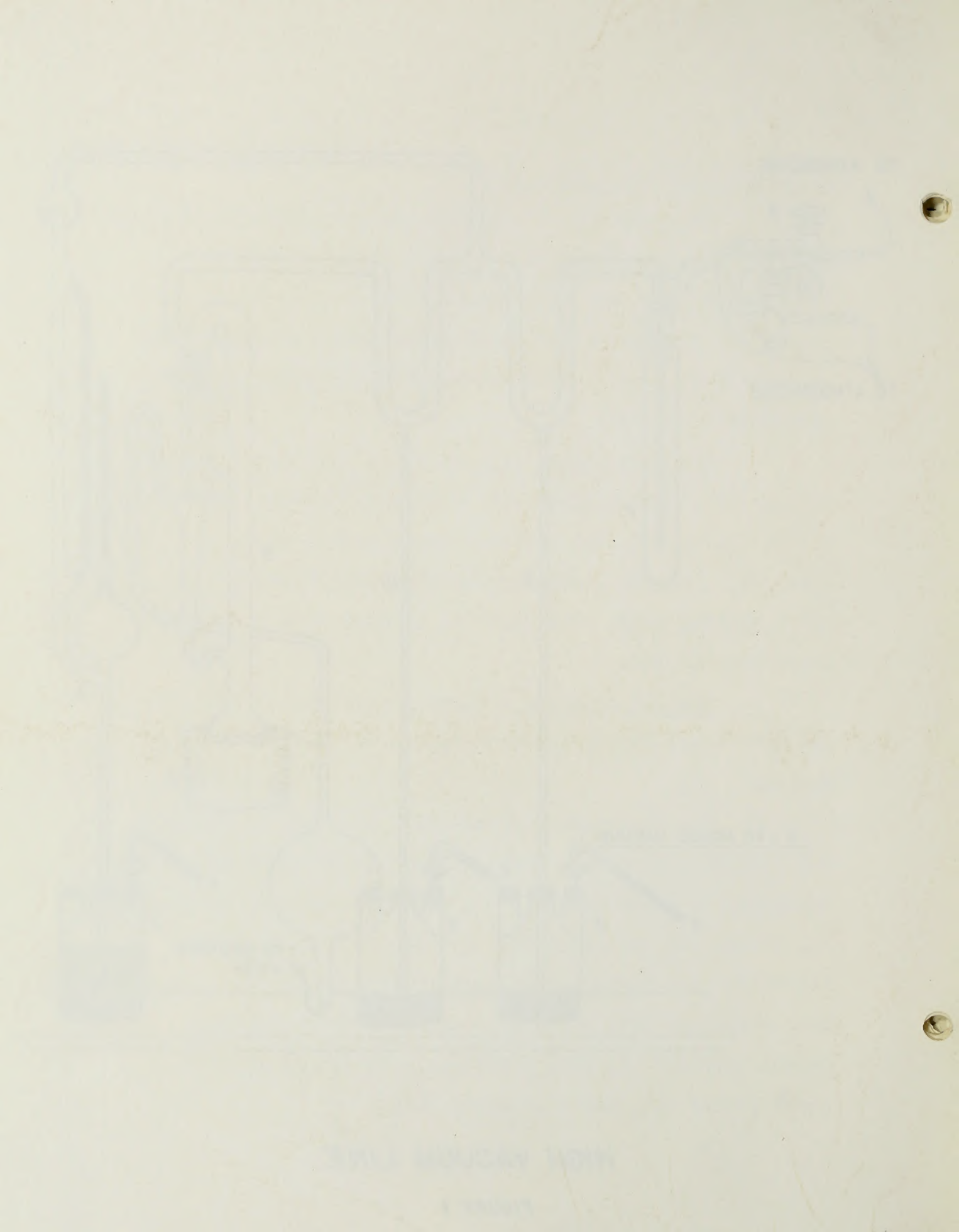
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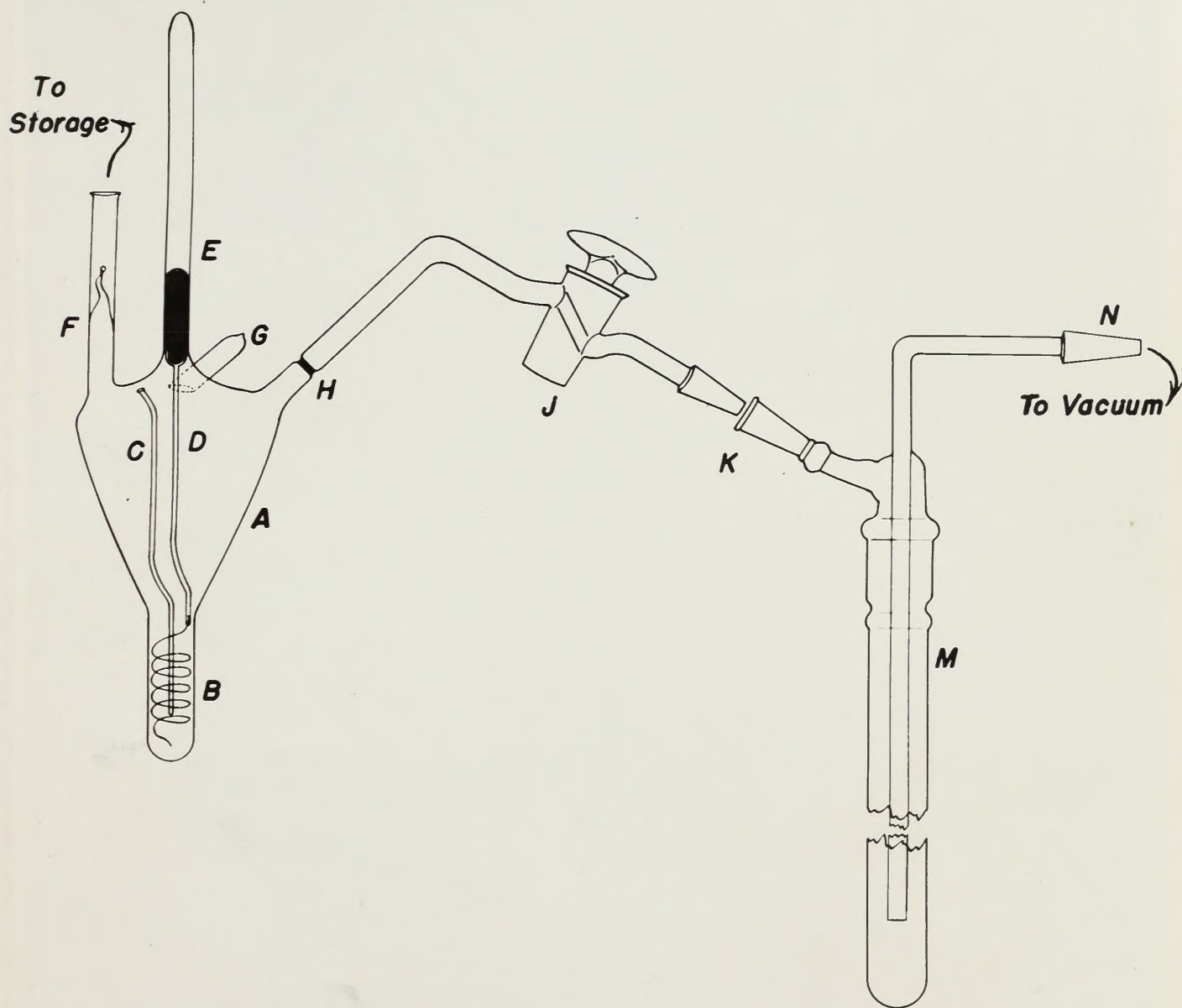
The fractional crystallizer is shown in Figure 2, and consisted of a pear shaped flask (A) of about 100 cc. capacity, to whose narrow end a tube extension of about 25 cc. volume (B) was attached. A trap (M) completed the assembly. The flask was equipped with a thermocouple well (C), a stirrer (D), a stirrer support (E), an internal vacuum preskoff tip (F), a filling tube (G), a slanted glass filter (H), and a stopcock (I).



HIGH VACUUM LINE

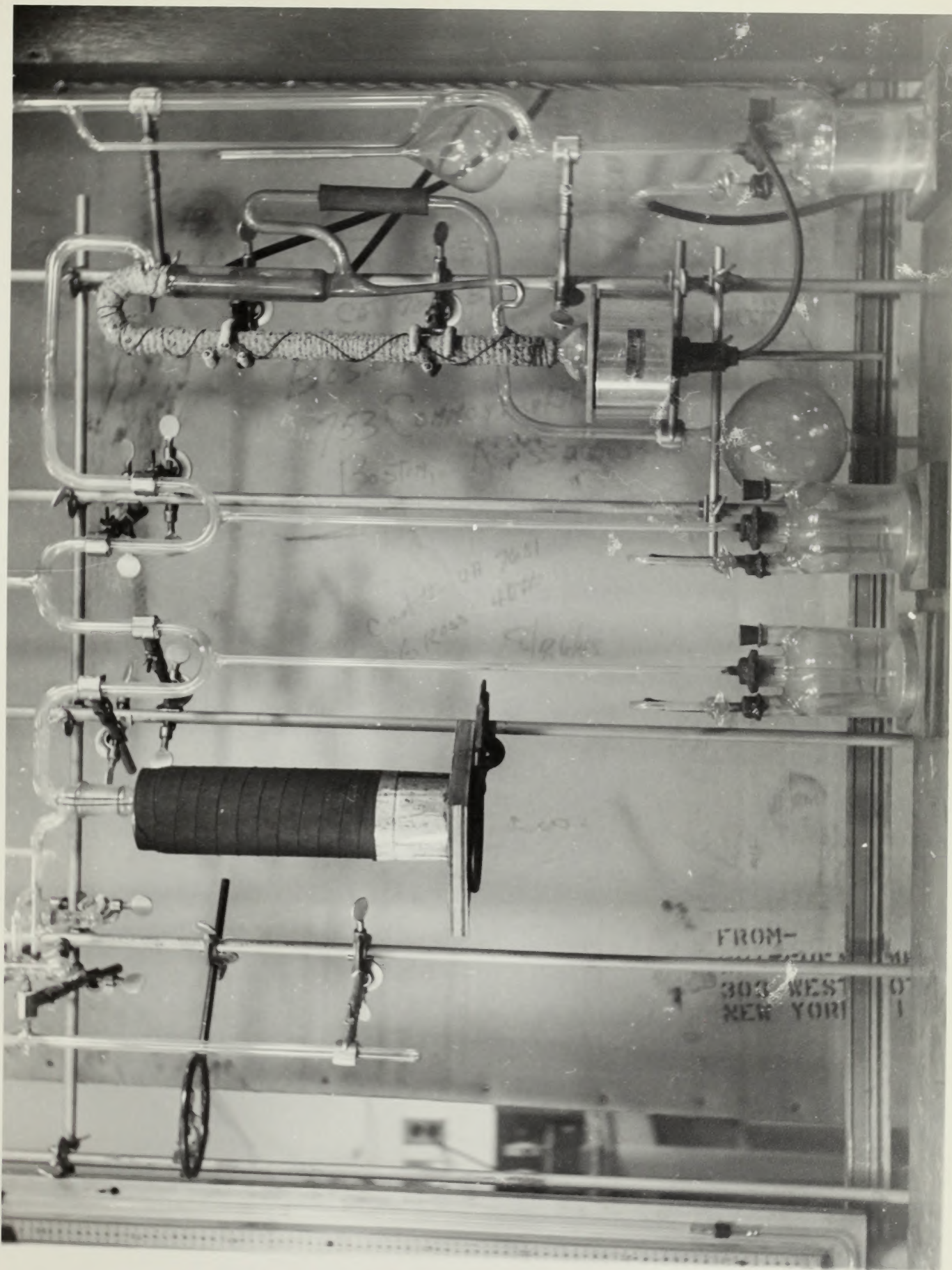
FIGURE 1





FRACTIONAL CRYSTALLIZATION APPARATUS

FIGURE 2



FROM-

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The thermocouple well was made of 3 mm. tubing and terminated about halfway down into the tube extension. It was centered as closely as possible in the tube and was sealed into the top of the crystallizer.

The stirrer was made of a coiled length of 14 gauge platinum wire sealed into 3 mm. rod. At the other end of the rod, a glass casing was attached which contained a length of soft iron rod. In operation, stirring was achieved by use of a solenoid activated by a current interrupter.

The sintered glass filter was 10 mm. in diameter, coarse grade, made by Corning Glass Works. (J) was a 6 mm. bore solid core stopcock. Internal vacuum breakoff tips were made according to the method described by Mair, et al. (17).

The sample storage manifold is shown in Figure 3.

Thermostat "A" (bulb thermostat) is shown in Figure 4. The thermostat was an iron tub with a rounded bottom. The tub rested in a plywood box, and the interspace between tub and box was packed with rockwool. The thermostat was equipped with a stirring chimney (A), a stirrer (B), a heater coil (C), an auxiliary heater (D), a cooling coil (E), and a mercury thermoregulator (F). The head of the Thermoregulator is shown in Figure 5, and the thermostat circuit is shown in Figure 6. The latter is controlled by a standard relay, manufactured by the Sargent Instrument Co.

Thermostat "B" (burette thermostat) is shown in

The thermocouple wire was made of 2 mm. tubing and terminated about halfway down into the tube extension. It was connected as closely as possible to the tube and was sealed into the top of the crystallizer.

The crystal was made of a cooled-tempered glass. The crystal wire was sealed into 5 mm. tube. The other end of the rod, a glass seal, was attached which contained a length of solid line rod. In operation, sealing was achieved by use of a solenoid actuated by a current transformer.

The tapered glass filter was 10 mm. in diameter, coarse grade, made by Corning Glass Works. It was 2 mm. bore solid cone stopcock. Internal vacuum breakoff tips were made according to the method described by Hall, et al. (1).

The sample storage manifold is shown in Figure 2. Thermostat "A" (oil thermostat) is shown in Figure

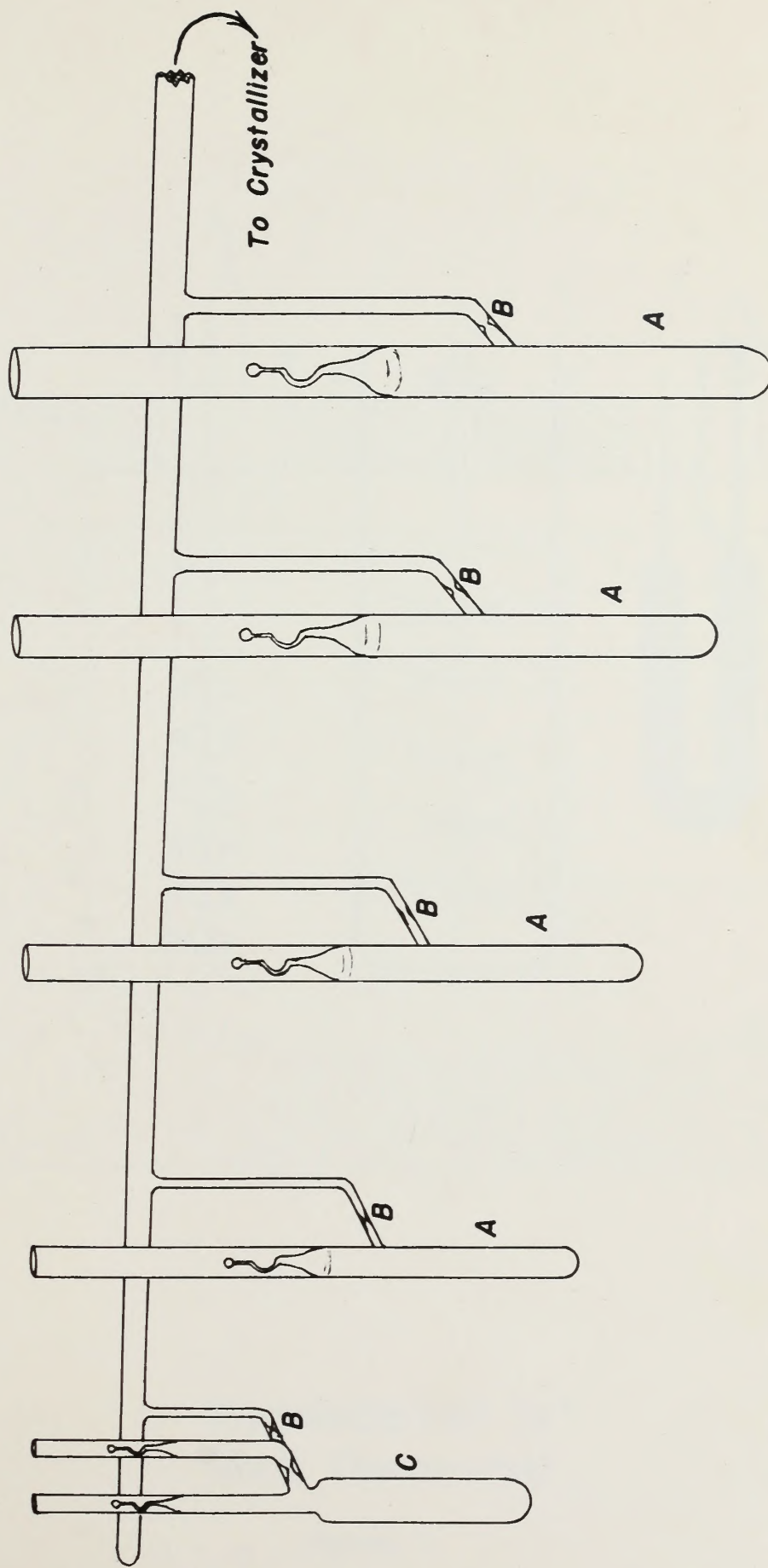
4. The thermostat was an iron tube with a rounded bottom. The top rested in a rigid box, and the interspace between the box and tube was packed with rockwool. The thermostat was equipped

with a stirring chimney (A), a stirrer (B), a heater coil (C), and auxiliary heater (D), a cooling coil (E), and a

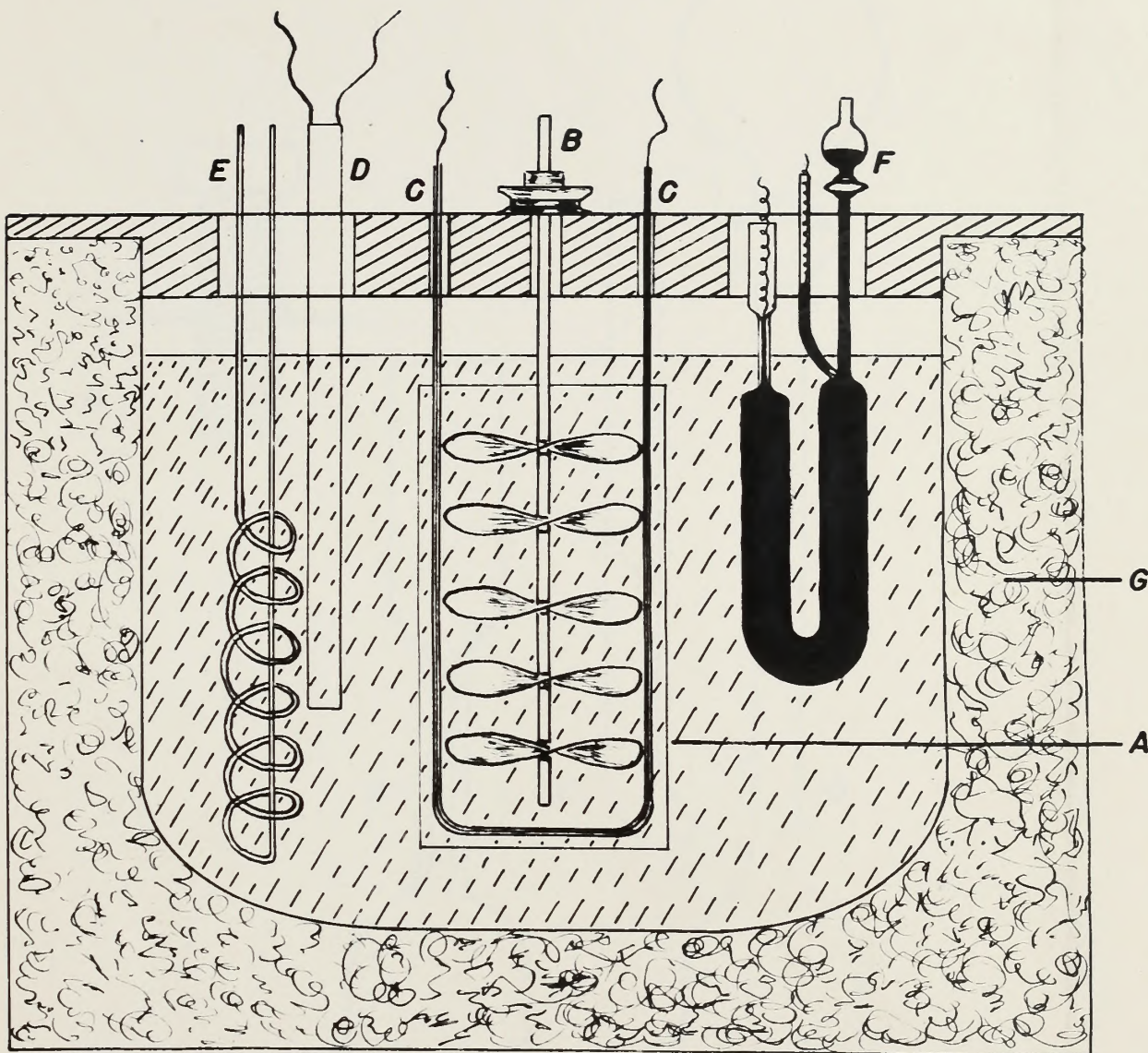
mercury thermometer (F). The head of the thermometer is shown in Figure 3, and the thermostat circuit is shown in

Figure 5. The latter is controlled by a standard relay, manufactured by the Sargent Instrument Co.

Thermostat "B" (oil thermostat) is shown in

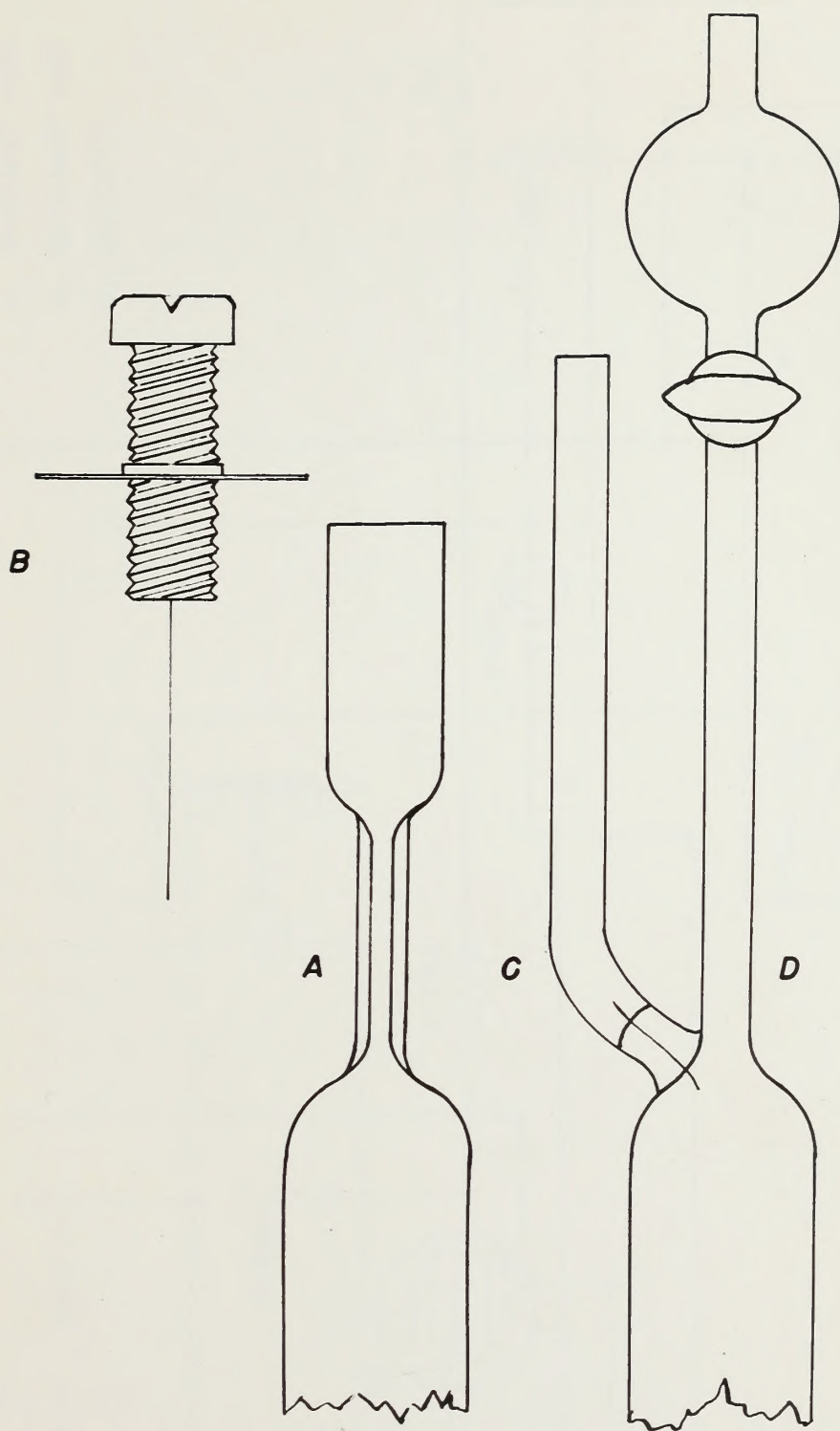


SAMPLE STORAGE MANIFOLD



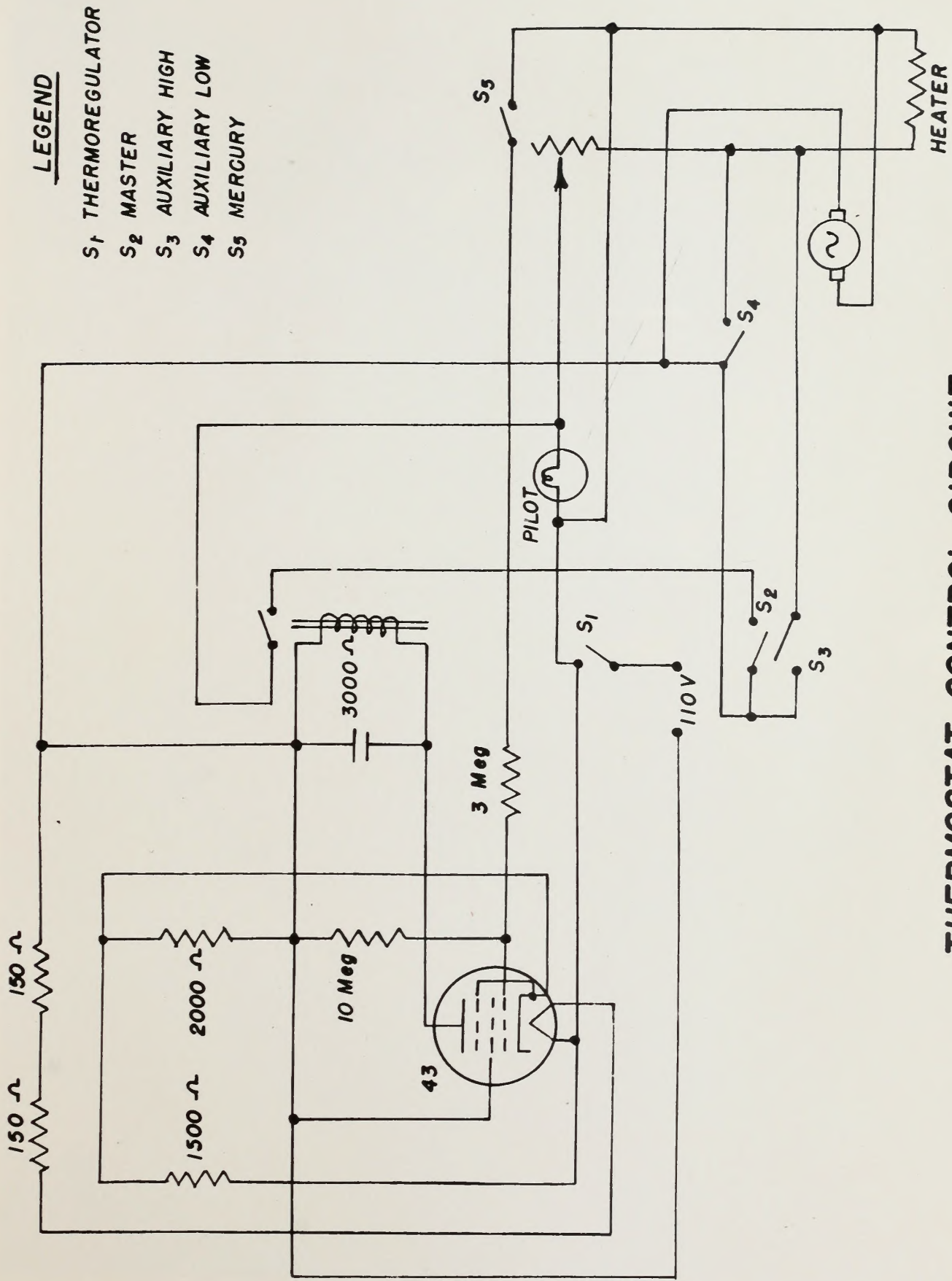
THERMOSTAT "A"
(Bulb Thermostat)

FIGURE 4



DETAIL OF HEAD OF THERMOREGULATOR

FIGURE 5

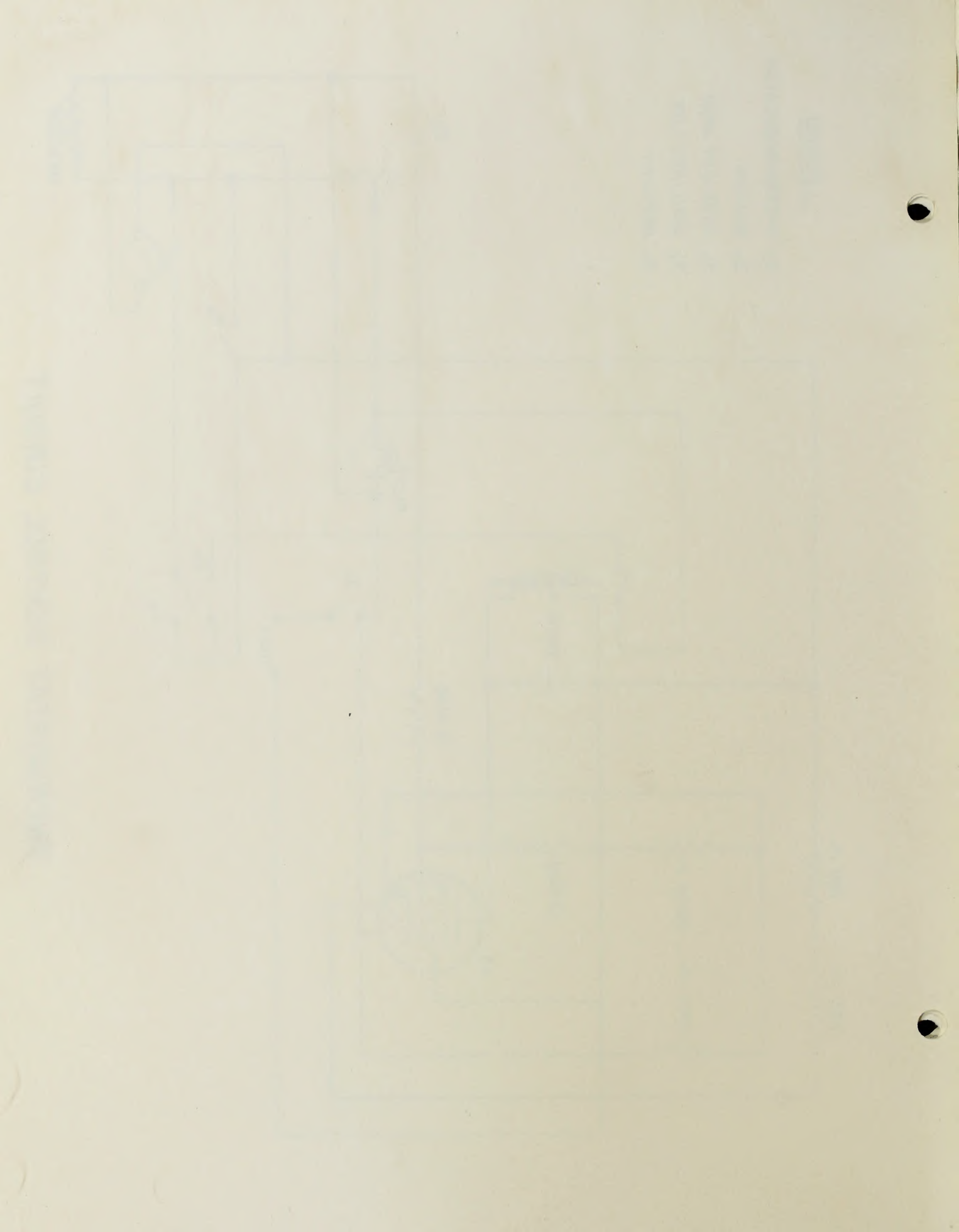


LEGEND

- S₁ THERMOREGULATOR
- S₂ MASTER
- S₃ AUXILIARY HIGH
- S₄ AUXILIARY LOW
- S₅ MERCURY

THERMOSTAT CONTROL CIRCUIT

FIGURE 6



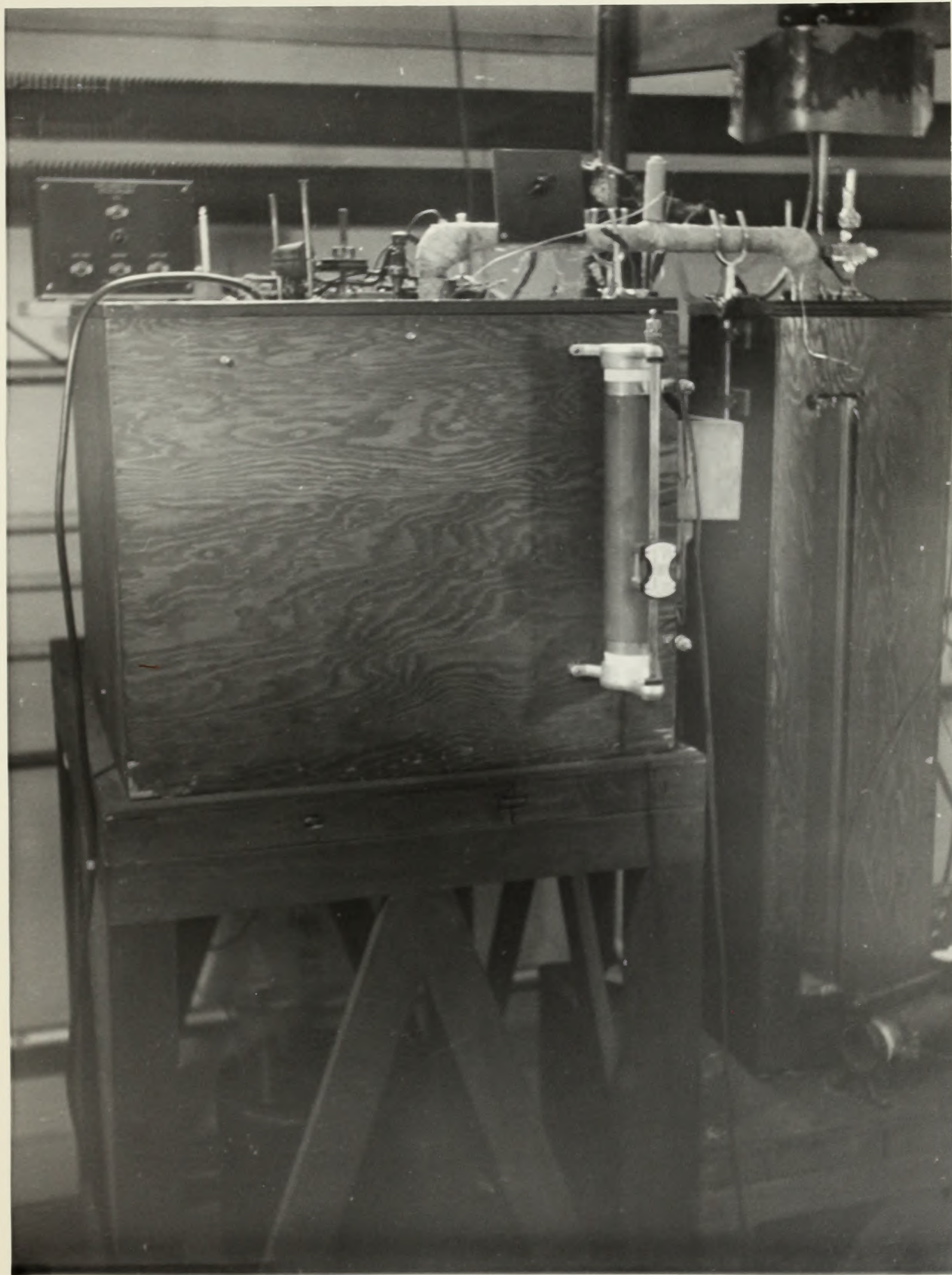


Figure 7. The thermostat was a glass test tube made of 4 inch tubing. It was mounted and fitted in a manner similar to that of thermostat "A", with the exception that the former was equipped with a viewing window through which measurements could be taken.

The bulb-and-burette assembly is shown in Figure 8.* The bulb (A- about 250 cc. volume) was connected through an arm (C) to the burette (B- a 60 cm. length of 4 mm. "trubore" tubing).

The connecting arm was equipped with nine glyptal coated copper-constantan thermocouples, fairly evenly spaced along the arm. The arm was then covered with a layer of asbestos tape, over which was placed a wrapping of aluminum foil. The aluminum foil was then coated with a layer of asbestos tape and the arm heater was laid on this layer of asbestos. Forty feet of nichrome wire, the resistance of which was 1.7 ohms/foot, was used. The heater was covered with a layer of asbestos tape, and the latter was wrapped with a layer of aluminum foil. The arm was finally wrapped with a $\frac{1}{4}$ inch layer of asbestos tape, and the latter was cemented in place with a coating of waterglass.

The electrical measuring equipment is shown in Figure 9. The equipment used consisted of a type K-2

*This apparatus has been described by Simons and Ritter (24).

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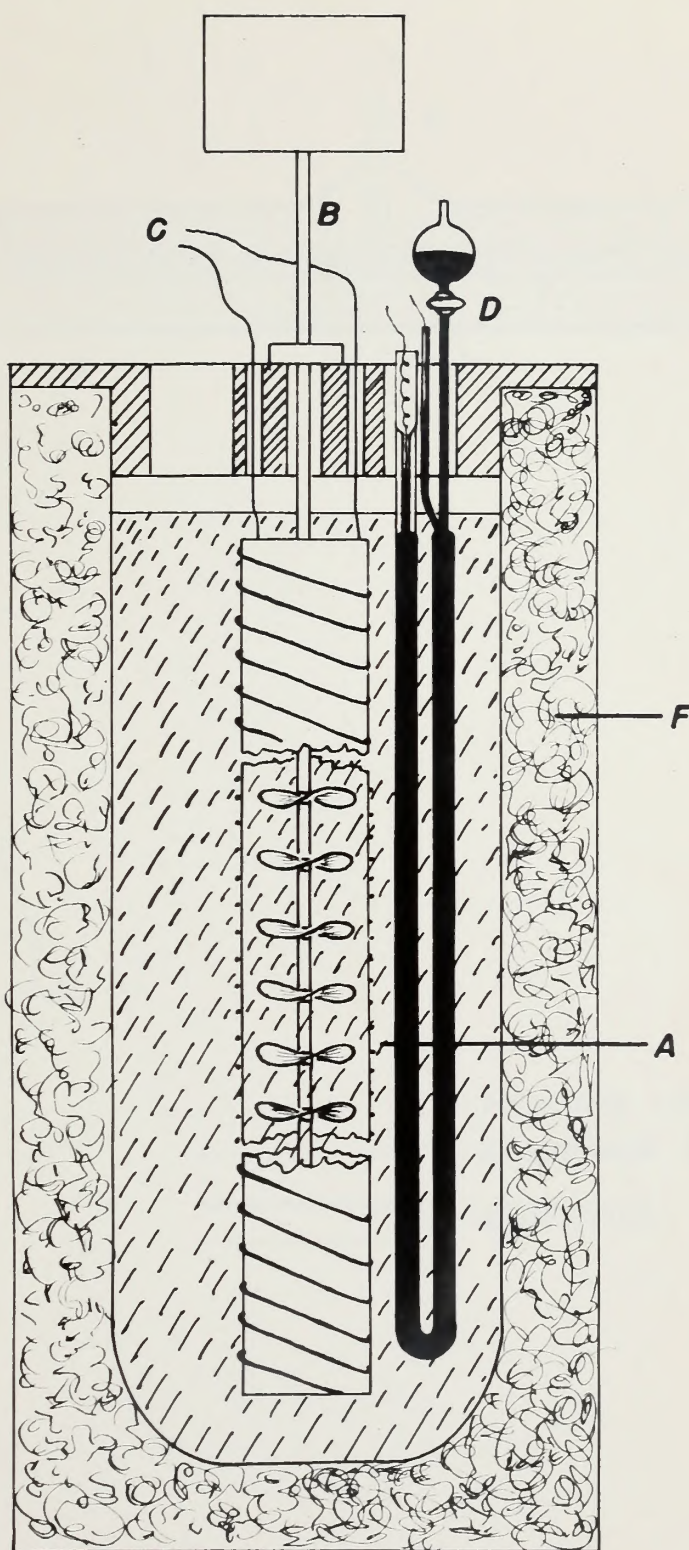
The bulb-and-burette assembly is shown in Figure 8.* The bulb (A - about 250 cc. volume) was connected through an arm (C) to the burette (B - a 60 cm. length of 4 mm. "fireproof" tubing).

The connecting arm was equipped with nine glyptal coated copper-constantan thermocouples, fairly evenly spaced along the arm. The arm was then covered with a layer of asbestos tape, over which was placed a wrapping of aluminum foil. The aluminum foil was then coated with a layer of asbestos tape and the arm heater was laid on this layer of asbestos. Forty feet of nichrome wire, the resistance of which was 1.5 ohms/foot, was used. The heater was covered with a layer of asbestos tape, and the latter was wrapped with a layer of aluminum foil. The arm was finally wrapped with a 1/4 inch layer of asbestos tape, and the latter was cemented in place with a coating of waterglass.

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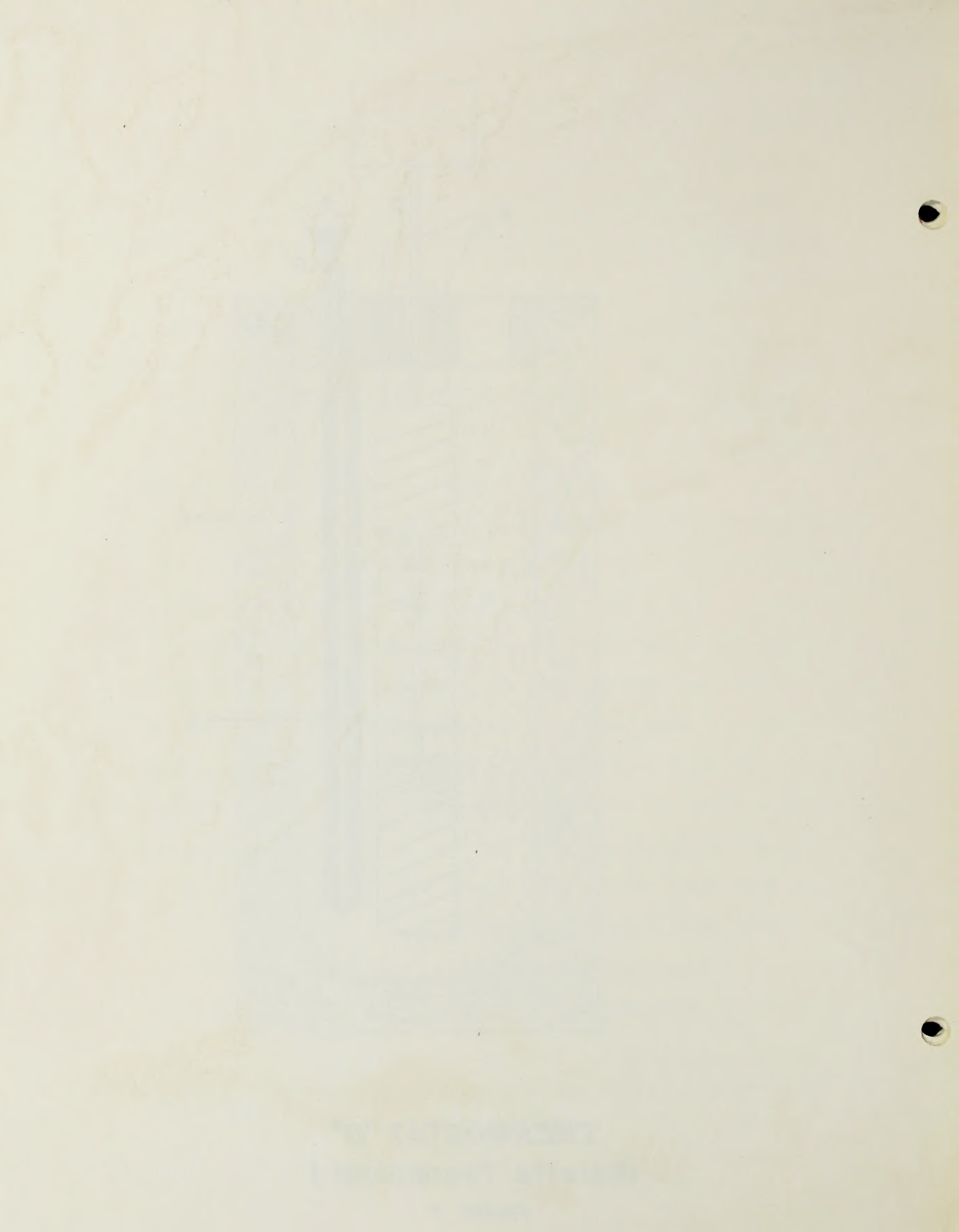
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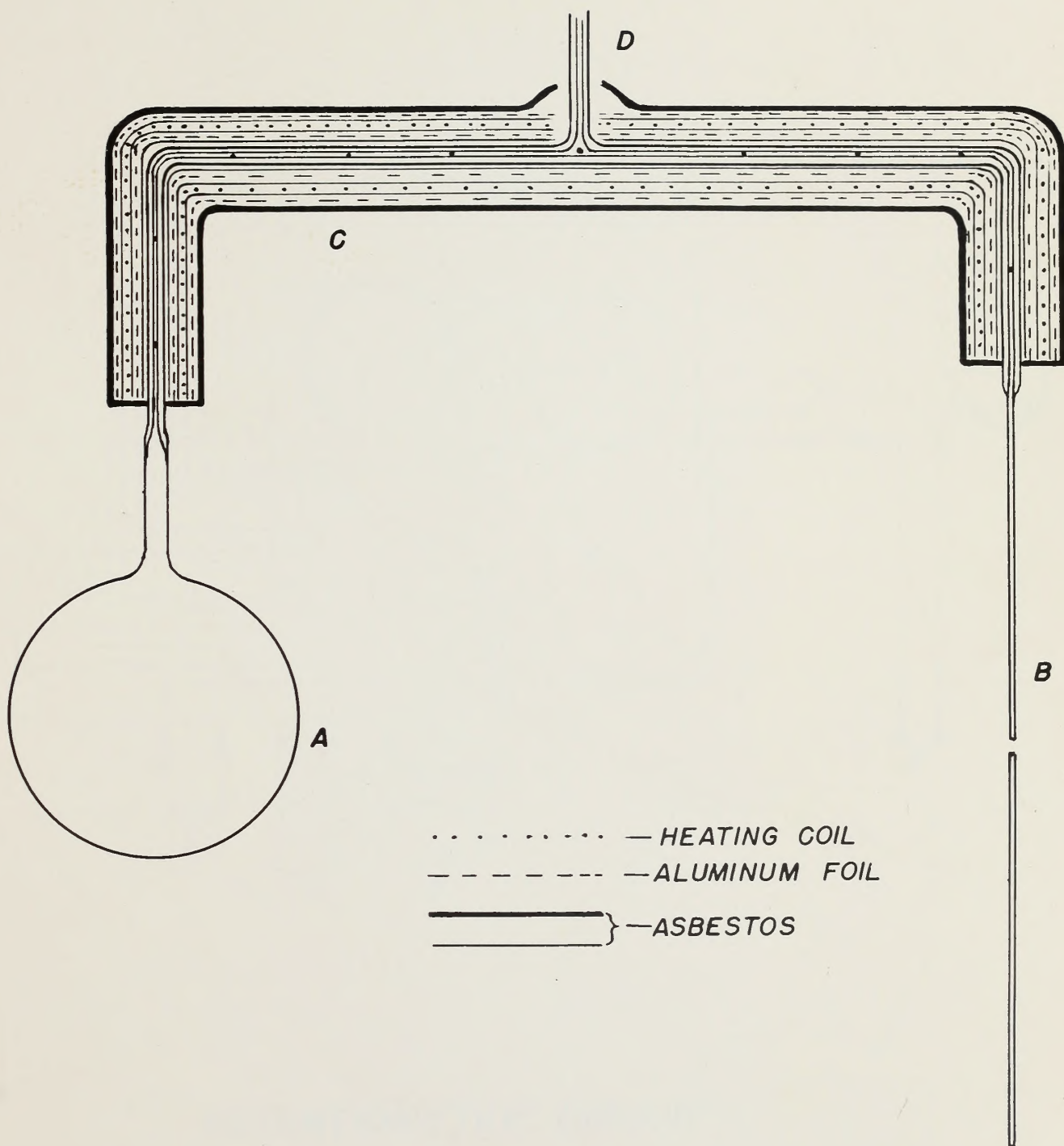
*This apparatus has been described by Simons and Ritter (24).



THERMOSTAT "B"
(Burette Thermostat)

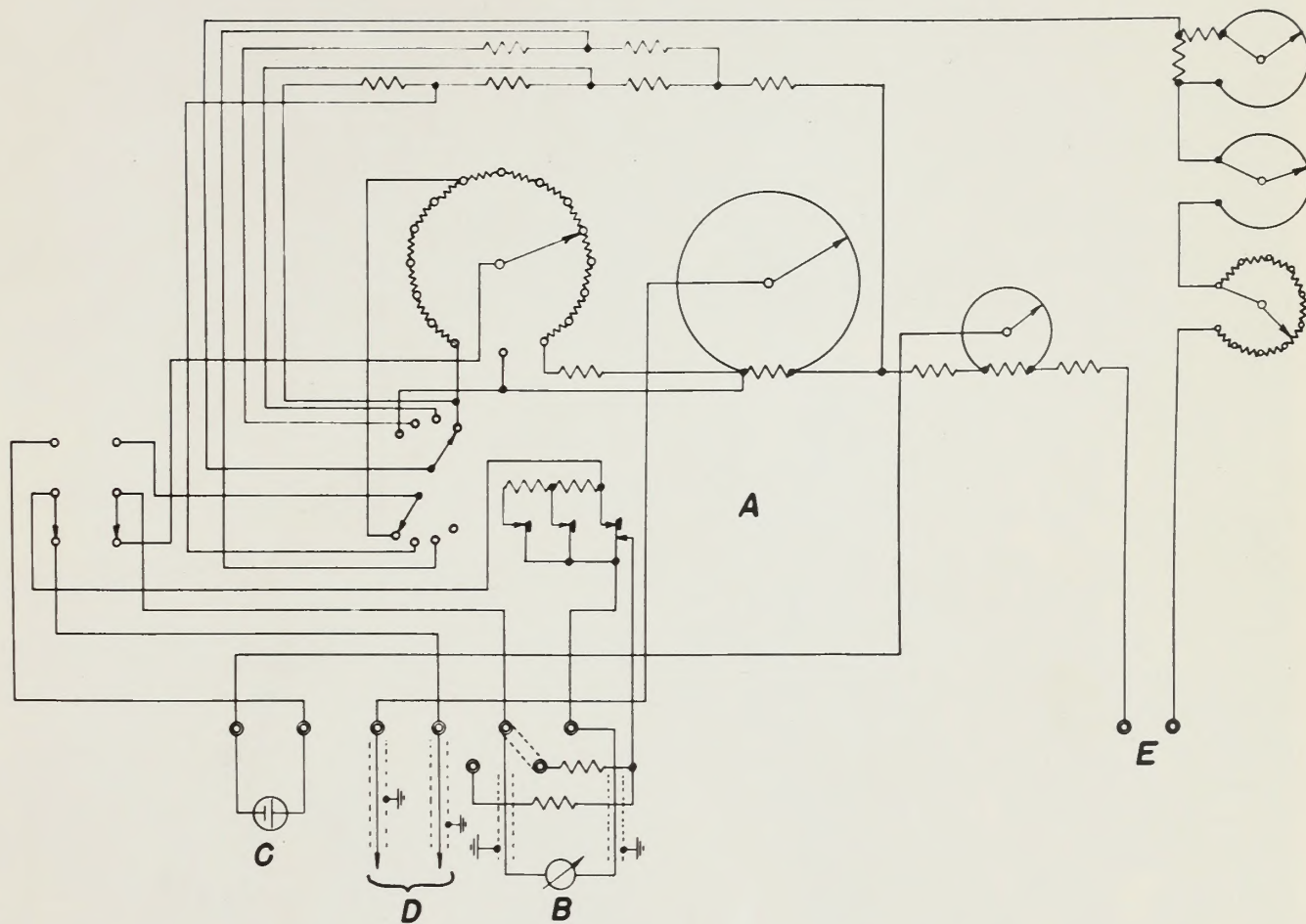
FIGURE 7





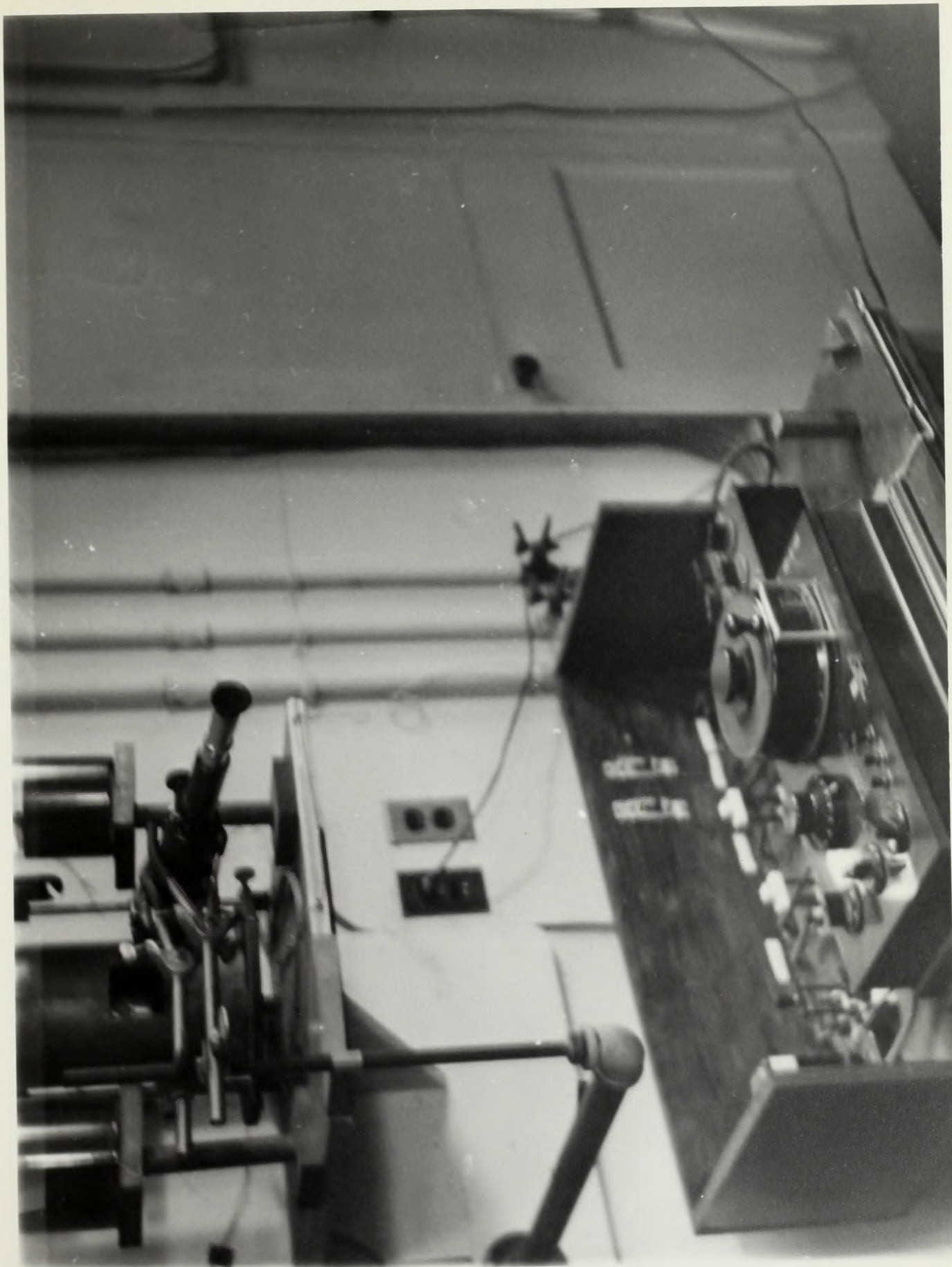
BULB AND BURETTE ASSEMBLY

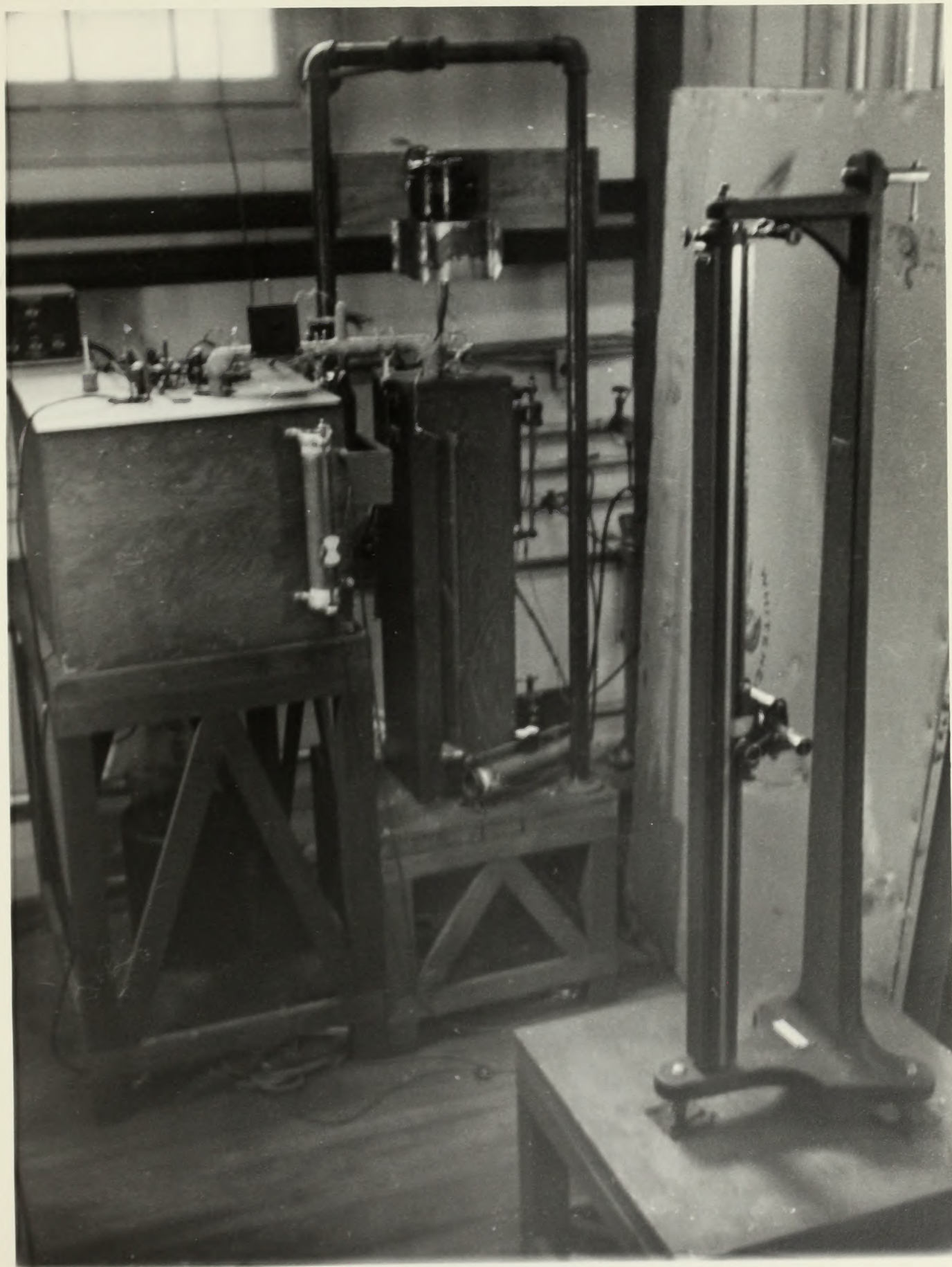
FIGURE 8



POTENTIOMETER CIRCUIT

FIGURE 9





potentiometer (A) manufactured by the Leeds and Northrup Co., a galvanometer (B), a standard cell (C), and a single junction copper-constantan thermocouple (D).

The galvanometer was produced by Leeds and Northrup, Catalogue No. 2500, and was matched to the potentiometer circuit. The galvanometer was enclosed in a cylindrical copper shield, and the latter was grounded. The galvanometer was mounted in a Julius suspension. Readings of the galvanometer deflection were taken through a 10 power telescope focussed on the galvanometer mirror in such a manner as to catch the reflection of an illuminated meter scale suspended 12 feet from the floor of the laboratory and 14 feet from the galvanometer. Such an arrangement yielded a sensitivity of 3 cm./ μ v.

The copper-constantan thermocouples were made of No. 36 B&S gauge copper wire and No. 30 B&S gauge constantan wire (1938 calibration) furnished by Leeds and Northrup. The thermocouple used in the purification work had soft soldered junctions; the thermocouples used to record thermostat temperatures were brazed. Leads from the thermocouples to the potentiometer were made of leaded cable, the casings of which were grounded.

Two storage batteries (E) were connected to the potentiometer through an external resistance. This circuit remained closed at all times to provide an even discharge rate of the batteries. The batteries were enclosed in an

potentiometer (A) manufactured by the Leeds and Northrup Co., a galvanometer (B), a standard cell (C), and a single junction copper-constantan thermocouple (D).

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Two storage batteries (E) were connected to the potentiometer through an external resistance. This circuit remained closed at all times to provide an even discharge rate of the batteries. The batteries were enclosed in an

insulated box to minimize the effect of temperature change of the surroundings on the output of the batteries.

Burette heights were read by means of a Gaertner cathetometer, equipped with a 100 cm. scale. The cathetometer could be read directly to millimeters and was provided with a vernier which gave readings to ± 0.005 cm. The cathetometer was mounted on a concrete block sunk through the floor.

The liquid density of trifluoroacetic acid was determined by use of a dilatometer, which is shown in Figure 10. This consisted of a bulb of approximately 1.5 cc. capacity, blown to a length of 1 mm. diameter "trubore" capillary tubing.

CONTENTS

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could be read directly to millimeters and was provided with a vernier which gave readings to ± 0.05 cm. The catheterometer

was mounted on a concrete block some through the floor.

The liquid density of trinitroresorcinol was

determined by use of a dilatometer, which is shown in Figure

10. This consisted of a bulb of approximately 1.5 cc.

capacity, blown to a length of 1 mm. diameter "taper"

capillary tubing.

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A-F



DILATOMETER

FIGURE 10

Purification of Trifluoroacetic Acid.

The acid used in this research was obtained as the sodium salt from the Columbia Chemical Co., Columbia, S. C. The salt, as received, was a gray, microcrystalline, slightly hygroscopic powder.

The free acid was obtained by treatment with sulfuric acid. Sodium trifluoroacetate was placed in a flask equipped with a condenser and a dropping funnel. Three times the theoretical amount of 95% sulfuric acid was added dropwise; the reaction mixture was held at about 10°. The reaction proceeded rapidly and was accompanied by a large evolution of heat. On completion of the sulfuric acid addition, a dark red liquid was obtained. Distillation of the free acid yielded a red product boiling over a range from 50-90°. When the distillation was conducted at atmospheric pressure, yields varying from 40-60% were obtained. Distillation at 5 mm. pressure produced a 95% yield of the impure free acid.

Investigation showed that the red color was due to the presence of elemental iodine. The impurity was removed by fractional distillation, carried out in a two foot, vacuum jacketed Vigreux column (theoretical plates unknown). It was found that most of the iodine came over in a low-boiling forerun between 52° and 70°. On the last fractionation, the acid was divided into three portions, and the middle cut was

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The free acid was obtained by treatment with sulfuric acid. Sodium trifluoroacetate was placed in a flask equipped with a condenser and a dropping funnel. Three times the theoretical amount of 98% sulfuric acid was added dropwise; the reaction mixture was held at about 10°. The reaction proceeded rapidly and was accompanied by a large evolution of heat. On completion of the sulfuric acid addition, a dark red liquid was obtained. Distillation of the free acid yielded a red product boiling over a range from 50-90°. When the distillation was conducted at atmospheric pressure, yields varying from 40-60% were obtained. Distillation at 5 mm. pressure produced a 95% yield of the impure free acid.

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used in the subsequent fractional crystallizations. The middle cut boiled at 71.71°C. (corr.), and consisted of 68 cc. of clear, water white liquid.

The theory underlying purification by fractional crystallization is based on the principle that slow freezing of a liquid containing some impurity will tend to concentrate the impurity in the liquid phase provided solid solutions are not formed. Therefore, by drawing off the mother liquor, some purification is effected. Information as to the degree of purity attained is given by taking freezing points on the material left in the crystallizer after removal of the mother liquor. A rise in freezing point indicates that the concentration of impurity has been lowered. This process of alternate crystallizations and freezing points is continued until no improvement of the freezing point is noted after two series of fractional crystallizations.

The acid was placed in the crystallizer, frozen to dry ice temperature, and the crystallizer was sealed off. The latter was then mounted on the vacuum line, and pumped for several minutes. The crystallizer was shut off from the pumping system, the acid was melted, then refrozen, and the crystallizer was pumped out again. This process was repeated four times to remove entrapped air. A freezing point was then taken. The crystallizer was fitted with an air jacket, and immersed in a freezing bath maintained at $-20 \pm 2^{\circ}\text{C.}$ The bath was stirred by bubbling air through it. The liquid acid

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was stirred and temperature readings were taken. Since trifluoroacetic acid displays a slight supercooling phenomenon, the point at which crystals first appear was easily detectable. The temperature at this point was taken as the true freezing point of the acid in that stage of purification. The run was considered at an end when the stirrer was frozen in.

The crystallization technique employed involved slow freezing of the acid till about 90% had solidified, and then filtering off the mother liquor. The crystallizer was immersed in a freezing bath held at $-18 \pm 2^{\circ}\text{C.}$, and the acid was stirred by swirling the crystallizer in the bath. When about 90% of the acid was frozen, the crystallizer was connected to the cold trap, the trap was pumped out, the crystallizer was inverted, the stopcock was opened, and the mother liquor was drawn off into the trap.

A total of eight crystallizations were done in three series. The first series consisted of three crystallizations in which 9 cc., 4 cc., and 2 cc., respectively were drawn off. Then a freezing point was taken. The second series consisted of three crystallizations, in which 3 cc., 4 cc., and 3 cc., respectively, were filtered off. Then a freezing point was taken. The third series consisted of two crystallizations in which 2 cc., and 3 cc., respectively, were removed. Then a freezing point was taken. These data are presented in Tables 22-25 (Appendix I).

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The freezing point had not changed sensibly after the first series of crystallizations. Therefore, it was concluded that the acid had been purified as well as possible with the available apparatus. The freezing point was found to be $-15.20 \pm 0.01^{\circ} \text{C}$. The only reported literature value (26) is -15.25°C .

The degassing procedure was then repeated three times, and the filter arm was sealed off. This was found to be a necessary precaution, since trifluoroacetic acid attacked stopcock grease. (The lubricants tested were Dow-Corning Silicone Grease, and A78-580, made by Eberbach and Son Co.)

The storage manifold was then sealed to the internal vacuum breakoff tip, the purified acid was frozen to dry ice temperature, the tip was smashed, the whole system was reevacuated, and the acid was distilled under vacuum into the storage bulbs. When these bulbs were sealed off, both the acid in the bulbs and in the main reservoir were frozen to dry ice temperature.

The purification data are presented graphically in Figures 11 and 12.

The efficiency of the crystallizer was checked by repeating the purification procedure with acetic acid. The freezing point of the acetic acid rose from 15.60°C . ^{to 16.58°C .} (Pure acetic acid melts at 16.60°C . 27)

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FIGURE 11

INCREASE IN FREEZING POINT DUE TO
FRACTIONAL CRYSTALLIZATION

- — After no crystallizations
- △ — After three crystallizations
- — After six crystallizations
- ◇ — After eight crystallizations
(not plotted because it superimposes
curve obtained after three crystallizations)

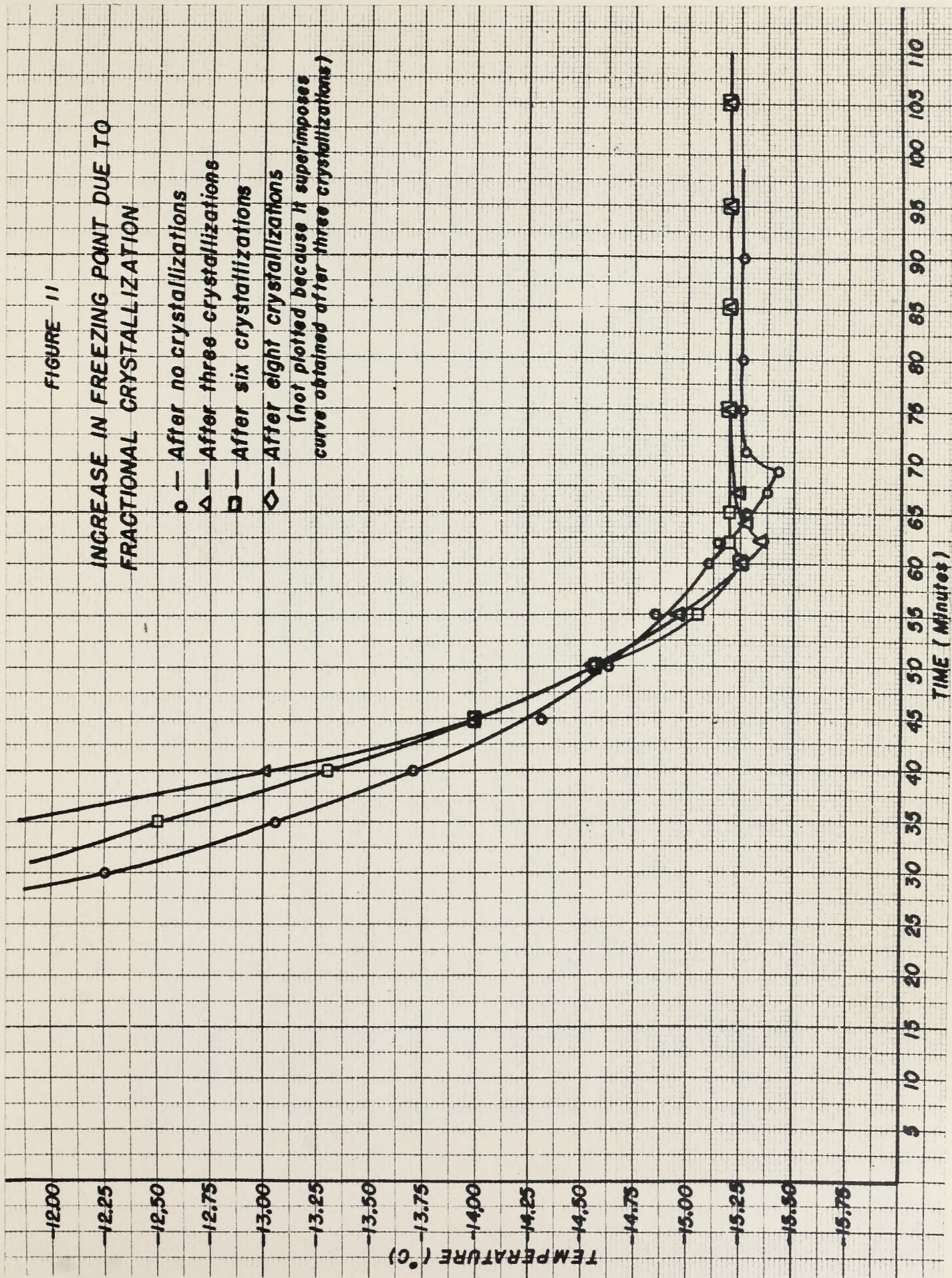
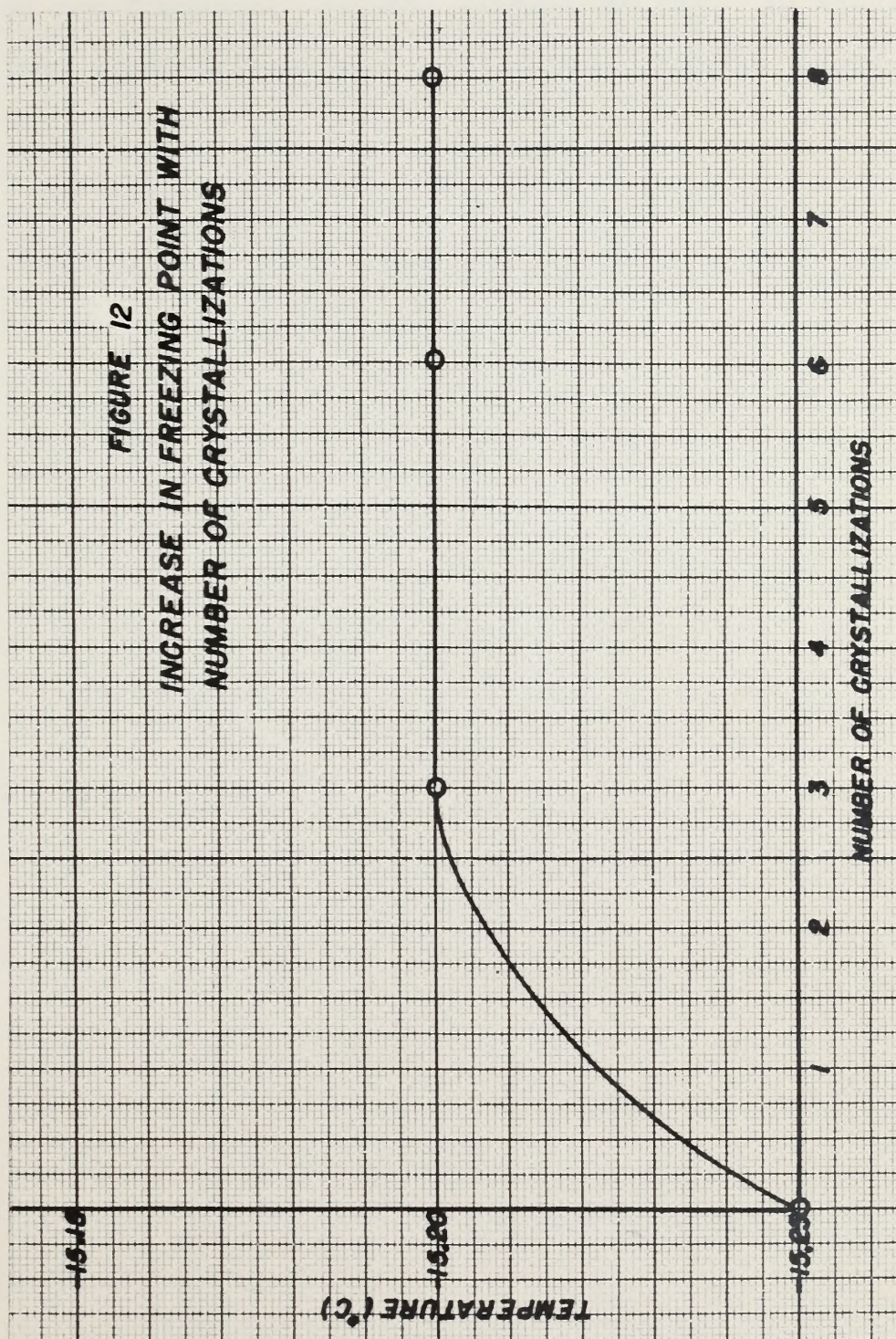


FIGURE 12
INCREASE IN FREEZING POINT WITH
NUMBER OF CRYSTALLIZATIONS



An analysis for fluorine was carried out (28).

Calculated for fluorine: 49.99%; found: 49.84%. An analysis for combined other halogen was carried out: Found: 0.00%.

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Determination of the Vapor Pressure of Trifluoroacetic Acid.

There is no information available in the literature concerning the vapor pressure of trifluoroacetic acid. The vapor pressure was therefore determined in an approximate manner. (It was felt that a more precise investigation lay outside the scope of this research.)

The vapor pressure was determined by means of a U-tube manometer made of 8 mm. tubing. Both sides of the manometer were connected through stopcocks to the high vacuum line; one side of the manometer was connected to a storage bulb equipped with an internal vacuum breakoff tip. Differences in mercury levels were read by means of the cathetometer.

Both sides of the manometer were evacuated for several hours; then, the stopcocks were closed and the mercury levels were read at intervals over a period of two hours with the cathetometer. No visible change was observed. The pressure in the manometer system just after evacuation, as measured by the McLeod gauge was 10^{-5} mm. The pressure at the end of the two hour period had dropped to 5×10^{-5} mm. It was felt that this was a good enough vacuum for the vapor pressure measurements.

The manometer arms were reevacuated for one hour, the stopcocks were then closed, the mercury levels were checked for equality, and the breakoff seal was smashed with

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The manometer arms were reevacuated for one hour, the stopcocks were then closed, the mercury levels were checked for equality, and the breakoff seal was smashed with

a magnetically actuated iron core encased in glass.

The acid was held at different temperatures by immersing the sample in a Dewar vessel containing water at the desired temperature. The water was stirred by means of a compressed air bubbler. The temperature of the thermostat bath was constant to $\pm 0.5^{\circ}$ C. Temperatures were measured with a 110° thermometer reading directly to one degree. The thermometer was checked against a calibrated thermometer and found to be accurate to $\pm 0.2^{\circ}$ C. in the range used.

It was not possible to obtain readings above room temperature, since the application of a bath at a temperature higher than that of the room set up, in effect, a vacuum distillation with the acid distilling out of the sample bulb and condensing on the walls of the system. The reading above 20° C. was obtained by using the room as an air thermostat and heating the room to higher temperatures.

Several readings were taken with the cathetometer at each temperature setting to check the precision. Each arm of the manometer was read alternately. The readings obtained with the cathetometer were accurate to only ± 0.01 cm. due to the instability of the cathetometer, which could not be mounted on the concrete block for this work.

The results obtained are presented in Table 2. With these data, $1/T$ and $\log_{10} p$ were calculated and these values are shown in Table 3. Figure 13 is a graphical repre-

a magnetically actuated iron core enclosed in glass.

The solid was held at different temperatures by

immersing the sample in a Dewar vessel containing water at

the desired temperature. The water was stirred by means of

a compressed air bubbler. The temperature of the thermo-

static bath was constant to $\pm 0.5^\circ \text{C}$. Temperatures were

measured with a 110° thermometer reading directly to one

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range used.

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values are shown in Table 3. Figure 13 is a graphical repre-

Table 2
Vapor Pressure of Trifluoroacetic Acid

Temperature (° C.)	Manometer Reading (mm.)		Manometer Reading (average) (mm.)		Vapor Pressure (mm.)
	Left Arm	Right Arm	Left Arm	Right Arm	
0	450.35	420.90	450.35	420.87	29.5
	450.35	420.85			
	450.35	420.85			
10	460.30	409.25	460.09	409.15	50.9
	460.05	409.25			
	460.05	409.05			
	460.00	409.05			
12	463.50	405.30	463.63	405.15	58.5
	463.65	405.15			
	463.75	405.00			
21	478.30	387.25	478.26	387.18	91.1
	478.30	387.15			
	478.20	387.15			
30	499.60	362.35	499.68	362.22	137.5
	499.75	362.05			
	499.70	362.25			

1962

1963

1964

1965

1966

1967

1968

418.80 384.12

419.20 384.12

420.00 384.30

421.30 402.00

422.30 402.10

423.00 402.20

424.00 404.00

425.00 404.00

426.00 404.20

427.00 404.20

428.20 420.80

429.00 420.80

430.00 420.80

431.00 420.80

432.00 420.80

433.00 420.80

434.00 420.80

435.00 420.80

436.00 420.80

437.00 420.80

438.00 420.80

439.00 420.80

440.00 420.80

27

418.20

384.10

27.1

18

422.00

402.10

28.2

19

426.00

404.10

29.6

0

420.00

420.80

38.2

(C.)

1966 YLR

1965 YLR

1964 YLR

1963 YLR

(C.)

дополнительно

перенесены расходы

(млн.)

перенесены расходы

Бюджет
Автоп

Лист 15 из 16 от 15.10.1968 г.

Лист 8

Table 3

 $1/T$ and $\log_{10} p$ as calculated from

Table 2

Temperature (C.)	Temperature (K.)	$\frac{1}{T} \times 10^3$ ($^{\circ}$ K.)	Pressure (mm.)	$\log_{10} p$
0	273.1	3.662	29.5	1.4692
10	283.1	3.532	50.9	1.7071
12	285.1	3.508	58.5	1.7669
21	294.1	3.403	91.1	1.9593
30	303.1	3.296	137.5	2.1383
71.7	344.8	2.900	760.0	2.8808

sentation of the data of Table 3 and was used to obtain the necessary vapor pressure information required in the subsequent calculations.

The accuracy of the experimentally determined vapor pressure is probably ± 1 mm. The accuracy of the vapor pressure obtained by using Figure ¹³20 ranges from ± 1 mm. at higher values of $1/T$ to ± 5 mm. at lower values of $1/T$ (that is, there is an error of 1% associated with the reading of the curve.

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Determination of the Liquid Density of Trifluoroacetic Acid.

There are no data available in the literature on the liquid density of trifluoroacetic acid. Such a determination was therefore carried out as a part of this research. The dilatometer used for this work has already been described.

The capillary was cleaned as follows. It was immersed in aqua regia for six hours, washed with one liter of distilled water, then soaked in cleaning solution for twelve hours and finally washed with three liters of distilled water. It was then rinsed with successive portions of 100 cc. each of Baker's C.P. analyzed acetone and ether, and sucked dry on the house vacuum. In the last step, the open end of the capillary was equipped with a dust trap made of a one foot length of 10 mm. tubing packed with glass wool.

The uniformity of bore of the capillary was checked in the following manner. A 10 cm. slug of mercury (triple distilled) was sucked into the capillary and held in place by a pinchclamp arrangement on either end of the capillary. Before use, the mercury was sprayed down a three foot column filled with a 1:5 nitric acid solution, after which it was shaken with ten 50 cc. portions of distilled water, two 50 cc. portions of acetone, and one 50 cc. portion of ether. Then it was pumped dry.

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checked in the following manner. A 10 cm. slug of mercury (triple distilled) was sucked into the capillary and held in place by a pinchcock arrangement on either end of the capillary. Before use, the mercury was sprayed down a three foot column filled with a 1:5 nitric acid solution, after which it was shaken with ten 50 cc. portions of distilled water, two 50 cc. portions of acetone, and one 50 cc. portion of ether. Then it was pumped dry.

The capillary was aligned with the vertical cross-hair in the cathetometer telescope, and readings of the length of the mercury slug were taken. Each reading overlapped the previous one. These data are presented in Table 26 (Appendix 1). Several readings were taken at each position of the slug to check precision. Upper and lower readings were taken alternately. The length of the slug was found to be essentially uniform (± 0.01 cm.). The diameter of the capillary was calculated to be 1.000 ± 0.001 mm.

A calibrating scratch was marked at the top and bottom of the capillary with a diamond tool. The capillary was almost completely filled with mercury, mounted in a vertical position, and the distance between the scratches, and the length of the mercury column were measured. These data are recorded in Table 27 (Appendix 1). Then the mercury was weighed, and the capillary volume was calculated.

A bulb was blown to one end of the capillary; the other end was fitted with a male joint. It was capped with a female and weighed. The dilatometer was then attached to a female mounted on a manifold. A test tube was charged with about 10 cc. of distilled water and attached to the manifold. The assembly was connected to the high vacuum line and pumped out after the water was frozen to dry ice temperature. The water was degassed several times, and water was distilled into the dilatometer to a point above the reference scratch at the bulb end of the capillary. Distillation was stopped

(24)

The capillary was aligned with the vertical cross-

hair in the cathetometer telescope, and readings of the length of the mercury slug were taken. Each reading overlapped the previous one. These data are presented in Table 28 (Appendix I). Several readings were taken at each position of the slug to check precision. Upper and lower readings were taken alternately. The length of the slug was found to be essentially uniform (± 0.01 cm.). The diameter of the capillary was calculated to be 1.000 ± 0.001 mm.

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by bringing the system to atmospheric pressure; then the dilatometer was removed from the system, immediately capped, and mounted and leveled vertically. The distance between the meniscus of the liquid and the reference scratch was then measured. These data are recorded in Table 28 (Appendix 1). The temperature was read with a 110° thermometer accurate to $\pm 0.2^{\circ}$. The dilatometer was then weighed and the volume of the bulb up to the reference scratch was calculated. This calculation is included in Table 28.

The dilatometer was emptied by pumping out the water, and was then evacuated for several hours to ensure drying. It was then mounted on a manifold which was connected to a storage bulb, and the whole system was joined through a stopcock to the high vacuum line. The manifold was evacuated for several hours, and the pressure in the system was read; the apparatus was closed off from the pumping units and the pressure was taken again at the end of one hour. In that period, the pressure had risen from 10^{-5} to 2×10^{-5} mm., which was considered to be sufficient evidence that the system was leakproof.

The manifold was reevacuated for an hour, and then shut off from the high vacuum line. The breakoff tip on the storage bulb was smashed after the acid in the bulb had been frozen to dry ice temperature. The acid was melted and a sufficient quantity was distilled into the dilatometer to fill it to a point just above the bulb calibration scratch.

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The acid in the dilatometer and in the storage bulb were frozen simultaneously to dry ice temperature, the system was opened to the vacuum line, and the dilatometer was sealed off at the upper reference scratch. The dilatometer was then weighed.

The dilatometer was mounted in a wire gauze support, and was suspended in thermostat "B" by means of thin copper wire. It was aligned with the vertical by its own weight (checked against the vertical crosshair of the cathetometer telescope.) The thermostat^{*} was then set at progressively higher temperatures and the distance between the reference scratch and the meniscus was measured with the cathetometer. These data are presented in Table 29 (Appendix 1).

It was now possible to calculate the liquid density of trifluoroacetic acid. In the calculations, corrections were made for the thermal expansion of the bulb and capillary and for the mass of the vapor in the space in the capillary above the liquid.^{**} As an example of the procedure, consider the data obtained at 51.79° C:

* In all thermostat work, the following procedure was generally adhered to. After the first indications that temperature control had been achieved, no readings were taken for 15 minutes. Then at least three separate temperature readings and three separate cathetometer readings were taken at ten minute intervals. If the readings remained constant, it was assumed that a satisfactory state of thermal equilibrium had been attained. If the readings were not constant, the process was repeated.

**No meniscus correction was made either here or in the dilatometer calibration as it was deemed insignificant.

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*The meniscus correction was made either here or in the dilatometer calibration as it was deemed insignificant.

the volume of the bulb to the reference mark at

$$27.8^{\circ} = 1.6558 \text{ cc.}$$

\therefore at 51.79° , the volume to the mark = (1.6558)

$$\left[1 + (51.79 - 27.8)(25 \times 10^{-6}) \right] = 1.6568 \text{ cc.}$$

the volume of the capillary at $24.2^{\circ} = 7.4514 \times 10^{-3}$

cc./cm.

\therefore at 51.79° , the volume = (7.4514×10^{-3})

$$\left[1 + (51.79 - 24.2)(25 \times 10^{-6}) \right]$$

$$= 7.4565 \times 10^{-3} \text{ cc./cm.}$$

the length of the column of acid = $44.127 - 32.045$

$$= 12.082 \text{ cm.}$$

\therefore the volume of acid in the capillary =

$$(7.4565 \times 10^{-3})(12.082) = 0.0901 \text{ cc.}$$

and the volume occupied by the acid = $1.6568 + 0.0901$

$$= 1.7469 \text{ cc.}$$

.....

$$\frac{1}{T} = \frac{1}{273.16} - \frac{1}{51.79} = \frac{1}{324.95} = 3.077 \times 10^{-3}$$

from Figure 20, $\log_{10} p = 2.553$

$$\therefore p = 357 \text{ mm.}$$

$$\text{or, } p = 0.47 \text{ atm.}$$

the total length of the capillary = 27.242 cm.

\therefore the volume of the dead space = (7.4565×10^{-3})

$$(27.242 - 12.082) = 0.1130 \text{ cc.}$$

using the perfect gas equation,

$$w = \frac{pVM}{RT}$$

the volume of the bulb to the reference mark at

$$27.8^{\circ} = 1.8558 \text{ cc.}$$

∴ at 21.73°, the volume to the mark = (1.8558)

$$\sqrt[3]{1 + (21.73 - 27.8)(25 \times 10^{-6})} = 1.8558 \text{ cc.}$$

the volume of the capillary at 24.2° = 7.4514×10^{-3}

$$\text{cc./cm.}$$

∴ at 21.73°, the volume = (7.4514×10^{-3})

$$\sqrt[3]{1 + (21.73 - 24.2)(25 \times 10^{-6})}$$

$$= 7.4565 \times 10^{-3} \text{ cc./cm.}$$

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∴ the volume of acid in the capillary =

$$(7.4565 \times 10^{-3})(12.082) = 0.0901 \text{ cc.}$$

and the volume occupied by the acid = $1.8558 + 0.0901$

$$= 1.9459 \text{ cc.}$$

$$\frac{1}{T} = \frac{1}{273.15} \frac{1}{21.73} = \frac{1}{324.95} = 3.077 \times 10^{-3}$$

from Figure 20, log $p = 2.553$

$$\therefore p = 357 \text{ mm.}$$

$$\text{or, } p = 0.47 \text{ atm.}$$

the total length of the capillary = 27.245 cm.

∴ the volume of the dead space = (7.4565×10^{-3})

$$(7.4565 \times 10^{-3})(27.245 - 12.082) = 0.1130 \text{ cc.}$$

using the perfect gas equation,

$$w = \frac{pVM}{RT}$$

$$w = \frac{(0.47)(0.1130)(171.05)}{(82.05)(324.95)}$$

$$= 0.0003 \text{ gm.}$$

The total mass of trifluoroacetic acid = 2.4661 gm.

the mass of the acid as liquid = 2.4661 - 0.003 =

$$2.4658 \text{ gm.}$$

.....

and the liquid density $\rho = \frac{2.4658}{1.7469} = 1.4115 \text{ gm./cc.}$

In these calculations, no in vacuo corrections were applied to the weighings. Such an omission introduces a 0.07% error into the density.

In order to obtain the mass of the vapor in the dead space, the assumption was made that the vapor is 50% associated and that, therefore, the molecular weight is 171.05. Such an assumption introduces a maximum error of $\pm 0.0001 \text{ gm.}$ in the evaluation of the mass of the vapor, which causes an error of only 0.004% in the mass of the liquid; this is insignificant. This assumption was used throughout the liquid density calculations.

A summary of the results is presented in Table 14. The data are shown graphically in Figure 14.

An empirical equation representing the data was determined. In general, it is possible to obtain several equations of different types which will express the given data (25). In certain special cases, the data will suggest the equation that will best represent the relation correlating

$$w = \frac{(0.47)(0.130)(171.05)}{(87.05)(324.92)}$$

$$= 0.0003 \text{ gm.}$$

The total mass of trifluoroacetic acid = 2.4561 gm.

the mass of the acid as liquid = 2.4561 - 0.0003 =

$$2.4558 \text{ gm.}$$

$$\text{and the liquid density } \rho = \frac{2.4558}{1.7430} = 1.4113 \text{ gm./cc.}$$

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A summary of the results is presented in Table I.

The data are shown graphically in Figure 1a.

An empirical equation representing the data was

determined. In general, it is possible to obtain several

equations of different types which will express the given

data (25). In certain special cases, the data will suggest

the equation that will best represent the relation correlating

the observed values.

A procedure known as the method of differences is applicable to the data at hand. Let the observed values be (t_i, p_i) , $(i = 0, 1, 2, \dots, n)$. The first differences are defined by the expression

$$\Delta p_i = p_{i+1} - p_i$$

the second differences are given by

$$\Delta^2 p_i = \Delta p_{i+1} - \Delta p_i$$

and the k^{th} differences are defined as

$$\Delta^k p_i = \Delta^{k-1} p_{i+1} - \Delta^{k-1} p_i$$

If the t_i form an arithmetic progression, and if it can be shown that the r^{th} differences of the p_i are constant, then the relation connecting the variables is

$$p = a_0 + a_1 t + a_2 t^2 + \dots + a_r t^r \quad (1)$$

As a rule, a given set of data will not possess constant differences of any order, but the r^{th} differences will be sensibly constant. In this event, an equation of the type (1) will be a more or less valid approximation to the relation between the variables, depending on the degree of inconstancy among the r^{th} differences.

Using the data in Figure 14, an arithmetic progression of t_i and its corresponding p_i were obtained and the method of differences was applied. The results are shown in Table ~~15~~ 5. It will be noted that the first differences are essentially constant, and, as a first approximation, an adequate representation of the data would be provided by the

the observed values.

A procedure known as the method of differences is applicable to the data at hand. Let the observed values be (t_i, p_i) , $(i = 0, 1, 2, \dots, n)$. The first differences are defined by the expression

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and the r th differences are defined as

$$\Delta^r p_i = \Delta^r p_{i+1} - \Delta^r p_i$$

If the t_i form an arithmetic progression, and if it can be shown that the r th differences of the p_i are constant, then the relation connecting the variables is

$$(1) \quad p = a_0 + a_1 t + a_2 t^2 + \dots + a_r t^r$$

As a rule, a given set of data will not possess constant differences of any order, but the r th differences will be sensibly constant. In this event, an equation of the type (1) will be a more or less valid approximation to the relation between the variables, depending on the degree of inconsistency among the r th differences.

Using the data in Figure 14, an arithmetic pro-

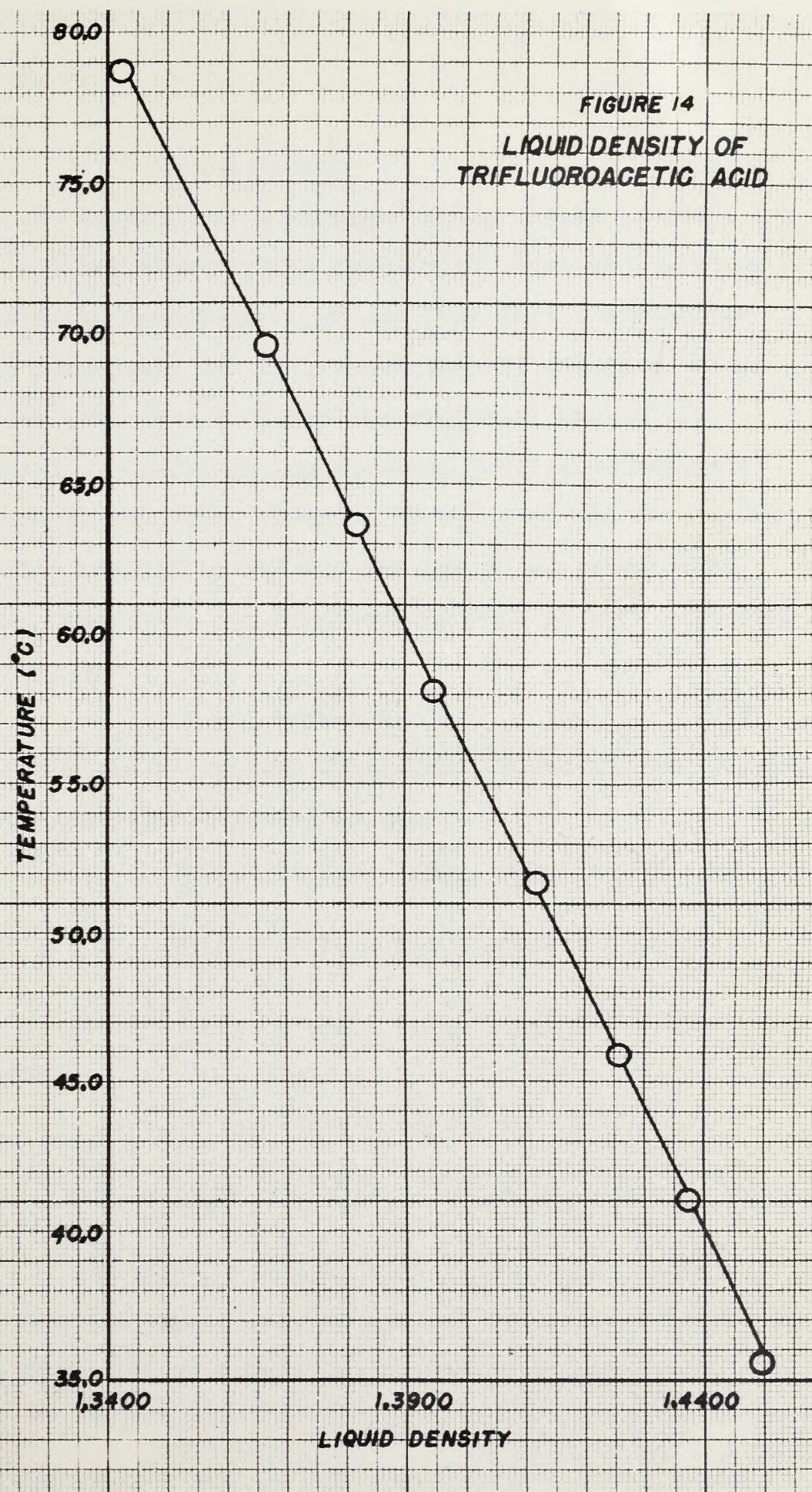
gression of t_i and its corresponding p_i were obtained and the method of differences was applied. The results are shown in Table IX. It will be noted that the first differences are

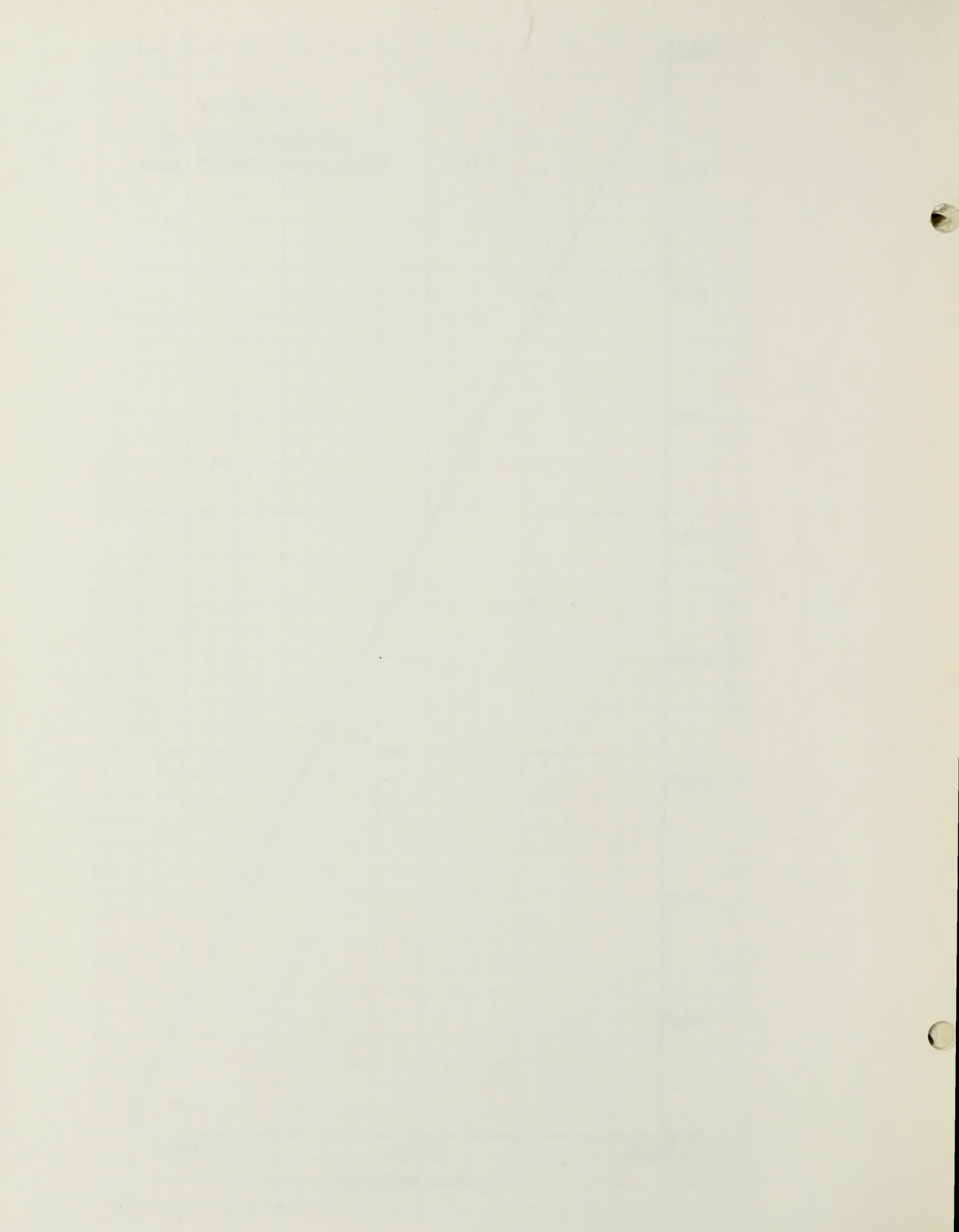
essentially constant, and, as a first approximation, an adequate representation of the data would be provided by the

Table 4
The Liquid Density of Trifluoroacetic Acid

Temperature (°C.)	Volume of bulb to mark (corr.)	Volume of Liquid in Capillary (corr.)	Volume of Liquid	Vapor Pressure mm.	Volume of Dead Space	Mass of Vapor in Dead Space	Mass of Liquid	ρ
35.78	1.6561	0.0445	1.7006	182	0.1585	0.0003	2.4658	1.4499
41.08	1.6563	0.0592	1.7155	229	0.1439	0.0003	2.4658	1.4374
45.96	1.6565	0.0729	1.7294	281	0.1302	0.0003	2.4658	1.4258
51.79	1.6568	0.0901	1.7469	357	0.1130	0.0003	2.4658	1.4115
58.30	1.6571	0.1104	1.7674	462	0.0928	0.0004	2.4657	1.3951
63.70	1.6573	0.1270	1.7843	569	0.0761	0.0004	2.4657	1.3819
69.65	1.6575	0.1464	1.8039	711	0.0568	0.0003	2.4658	1.3669
78.91	1.6579	0.1788	1.8367	982	0.0245	0.0002	2.4659	1.3426

FIGURE 14
LIQUID DENSITY OF
TRIFLUOROACETIC ACID





expression

$$p = a_0 + a_1 t \quad (2)$$

which is the equation of a straight line. This, however, will not suffice since visual inspection shows the curve of Figure 14 to be non-linear. It was felt that a correction factor to compensate for this non-linearity should be added to equation (2). Two such factors suggested themselves: $a_2 e^t$; or $a_2 t^2$. The latter was selected because it was felt that the deviation from linearity of the data did not increase sufficiently rapidly to warrant the use of an exponential function. Therefore, the equation selected as best representing the data was

$$p = a_0 + a_1 t + a_2 t^2. \quad (3)$$

The constants were determined by the method of least squares, which yielded the equations

$$\sum_{i=1}^8 (a_0 + a_1 t_i + a_2 t_i^2 - p_i) \cdot 1 = 0$$

$$\sum_{i=1}^8 (a_0 + a_1 t_i + a_2 t_i^2 - p_i) \cdot t_i = 0$$

$$\sum_{i=1}^8 (a_0 + a_1 t_i + a_2 t_i^2 - p_i) \cdot t_i^2 = 0$$

Or rewritten,

$$8a_0 + \left(\sum_{i=1}^8 t_i\right)a_1 + \left(\sum_{i=1}^8 t_i^2\right)a_2 = \sum_{i=1}^8 p_i$$

$$\left(\sum_{i=1}^8 t_i\right)a_0 + \left(\sum_{i=1}^8 t_i^2\right)a_1 + \left(\sum_{i=1}^8 t_i^3\right)a_2 = \sum_{i=1}^8 p_i t_i$$

$$\left(\sum_{i=1}^8 t_i^2\right)a_0 + \left(\sum_{i=1}^8 t_i^3\right)a_1 + \left(\sum_{i=1}^8 t_i^4\right)a_2 = \sum_{i=1}^8 t_i^2 p_i$$

Substituting the appropriate summations (whose derivations are shown in Table 14) we obtain the system of simultaneous

expression

$$p = a_0 + a_1 t \quad (2)$$

which is the equation of a straight line. This, however, will not suffice since visual inspection shows the curve of Figure 14 to be non-linear. It was felt that a correction factor to compensate for this non-linearity should be added

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ing the data was

$$p = a_0 + a_1 t + a_2 t^2 \quad (3)$$

The constants were determined by the method of least

squares, which yielded the equations

$$\sum_{i=1}^n (a_0 + a_1 t_i + a_2 t_i^2 - p_i)^2 = 0$$

$$\sum_{i=1}^n (a_0 + a_1 t_i + a_2 t_i^2 - p_i) t_i = 0$$

$$\sum_{i=1}^n (a_0 + a_1 t_i + a_2 t_i^2 - p_i) t_i^2 = 0$$

Or rewritten,

$$n a_0 + a_1 \sum_{i=1}^n t_i + a_2 \sum_{i=1}^n t_i^2 = \sum_{i=1}^n p_i$$

$$\left(\sum_{i=1}^n t_i \right) a_0 + \left(\sum_{i=1}^n t_i^2 \right) a_1 + \left(\sum_{i=1}^n t_i^3 \right) a_2 = \sum_{i=1}^n p_i t_i$$

$$\left(\sum_{i=1}^n t_i^2 \right) a_0 + \left(\sum_{i=1}^n t_i^3 \right) a_1 + \left(\sum_{i=1}^n t_i^4 \right) a_2 = \sum_{i=1}^n p_i t_i^2$$

Substituting the appropriate summations (whose derivations are

shown in Table 14) we obtain the system of simultaneous

Table 5

Analysis of Liquid Density Data
Using Method of Differences

$t(^{\circ}\text{C})$	ρ	$\Delta\rho$
35.0	1.4519	-0.0120
40.0	1.4399	-0.0120
45.0	1.4279	-0.0110
50.0	1.4269	-0.0135
55.0	1.4034	-0.0124
60.0	1.3910	-0.0122
65.0	1.3788	-0.0128
70.0	1.3660	-0.0130
75.0	1.3530	-0.0131
80.0	1.3399	

Table 3
Analysis of Liquid Density Data
Using Method of Differences

$\Delta \rho$	ρ	$\rho (\text{g/cm}^3)$
-0.0120	1.4312	32.0
-0.0120	1.4332	34.0
-0.0110	1.4372	36.0
-0.0122	1.4392	38.0
-0.0124	1.4424	40.0
-0.0122	1.4510	42.0
-0.0128	1.4538	44.0
-0.0120	1.4560	46.0
-0.0120	1.4580	48.0
-0.0120	1.4600	50.0
-0.0121	1.4630	52.0
	1.4662	54.0

equations

$$8a_0 + (4.4517 \times 10^2)a_1 + (2.6297 \times 10^4)a_2 = 11.2111$$

$$(4.4517 \times 10^2)a_0 + (2.6297 \times 10^4)a_1 + (1.6370 \times 10^6)a_2 = 6.2007 \times 10^2$$

$$(2.6297 \times 10^4)a_0 + (1.6370 \times 10^6)a_1 + (1.0200 \times 10^8)a_2 = 3.6420 \times 10^4$$

Solving, we have $a_0 = 1.5402$, $a_1 = -2.506 \times 10^{-3}$, and $a_2 = 1.863 \times 10^{-7}$; and the empirical equation is

$$\rho = 1.5402 - (2.506 \times 10^{-3})t + (1.863 \times 10^{-7})t^2$$

Employing this equation, one obtains results differing from the experimentally determined values by at most ± 0.0006 gm./cc. (Table 7).

equations

$$8a_0 + (4.4517 \times 10^{-2})a_1 + (2.6297 \times 10^{-4})a_2 = 11.211$$

$$(4.4517 \times 10^{-2})a_0 + (2.6297 \times 10^{-4})a_1 + (1.6370 \times 10^{-6})a_2 = 6.2007 \times 10^{-2}$$

$$(2.6297 \times 10^{-4})a_0 + (1.6370 \times 10^{-6})a_1 + (1.0200 \times 10^{-8})a_2 = 2.6420 \times 10^{-4}$$

Solving, we have $a_0 = 1.5402$, $a_1 = -2.806 \times 10^{-2}$, and $a_2 =$

1.863×10^{-7} ; and the empirical equation is

$$p = 1.5402 - (2.806 \times 10^{-2})t + (1.863 \times 10^{-7})t^2$$

Employing this equation, one obtains results differing from

the experimentally determined values by at most ± 0.006 mm.

cc. (Table V).

Table 6
Summation Data

$t (^{\circ}\text{C.})$	t^2	t^3	t^4	P	tP	t^2P
35.78	1280.2	45805.8	1,638,900	1.4499	51.878	1856.2
41.08	1687.6	69325.2	2,847,900	1.4374	59.046	2425.6
45.96	2112.3	97082.3	4,461,900	1.4258	65.529	3011.7
51.79	2682.2	138911.4	7,194,200	1.4115	73.103	3786.0
58.30	3398.9	198155.3	11,552,500	1.3951	81.335	4741.9
63.70	4057.7	258474.9	16,464,800	1.3819	88.028	5607.4
69.65	4851.1	337880.7	23,533,400	1.3669	95.205	6631.0
78.91	6226.8	491355.9	38,772,900	1.3426	105.942	8359.9
Summation						
4.4517 $\times 10^2$	2.6297 $\times 10^4$	1.6370 $\times 10^6$	1.0200 $\times 10^8$	11.2111	6.2007 $\times 10^2$	3.6420 $\times 10^4$

Table 7

Comparison of Experimentally Determined Liquid
Density with that Calculated by means of
the Empirical Equation

t ($^{\circ}\text{C.}$)	(gm./cc. (observed))	(gm./cc. (calculated))	Deviation
35.78	1.4499	1.4505	+0.0006
41.08	1.4374	1.4376	+0.0002
45.96	1.4258	1.4254	-0.0004
51.79	1.4115	1.4109	-0.0006
58.30	1.3951	1.3947	-0.0004
63.70	1.3819	1.3814	-0.0005
69.65	1.3669	1.3666	-0.0003
78.91	1.3426	1.3427	+0.0001

Table 7

Comparison of Experimentally Determined Liquid
Density with that Calculated by means of
the Empirical Equation

t ($^{\circ}\text{C.}$)	(gm./cc. (observed))	(gm./cc. (calculated))	Deviation
35.75	1.4439	1.4405	+0.0003
41.08	1.4374	1.4376	+0.0002
45.93	1.4338	1.4334	-0.0004
51.79	1.4113	1.4109	-0.0004
56.30	1.3931	1.3947	-0.0004
62.70	1.3819	1.3814	-0.0005
69.93	1.3669	1.3663	-0.0003
76.91	1.3526	1.3527	+0.0001

Determination of the Meniscus Correction.

If a liquid is able to wet the walls of a containing vessel, a meniscus will be formed whose shape, and, therefore, its volume, is a function of the temperature and of the surface tension (which, itself, is temperature dependent). If the meniscus volume is not corrected for, any calculated volume will be in error by that amount. Frequently (as in the liquid density calculations), the meniscus correction is a negligible term; sometimes it is not.

There are no data in the literature which will permit the calculation of the volume of the meniscus of trifluoroacetic acid. By use of suitable assumptions, an approximation may be made. First, it is necessary to assume that the interfacial contact angle between liquid and glass is 0° . Inasmuch as this is known to be the case for water, acetic acid, and trichloroacetic acid, it is felt that this assumption is justified. The second assumption is that the surface tension of trifluoroacetic acid is the same as that of trichloroacetic acid. This assumption is probably incorrect, but since an error of 20% in the value assigned for the surface tension would only lead to an error of ± 0.002 cc. in the volume of the meniscus (in a tube 4 mm. in diameter), this assumption is felt to be satisfactory for the purposes of this work. This assumption is felt to be acceptable, also inasmuch as acetic acid and trichloroacetic acid values for

Determination of the Meniscus Correction.

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There are no data in the literature which will permit the calculation of the volume of the meniscus of trichloroacetic acid. By use of suitable assumptions, an approximation may be made. First, it is necessary to assume that the interfacial contact angle between liquid and glass is 0°. Inasmuch as this is known to be the case for water, acetic acid, and trichloroacetic acid, it is felt that this assumption is justified. The second assumption is that the surface tension of trichloroacetic acid is the same as that of trichloroacetic acid. This assumption is probably incorrect, but since an error of 20% in the value assigned for the surface tension would only lead to an error of 0.002 cc. in the volume of the meniscus (in a tube 4 mm. in diameter), this assumption is felt to be satisfactory for the purposes of this work. This assumption is felt to be acceptable, also inasmuch as acetic acid and trichloroacetic acid values for

their respective surface tensions at comparable temperatures do not differ by more than 20%. The third assumption necessary is that $d\gamma/dT$ (where γ represents the surface tension) is the same for acetic acid, trichloroacetic acid, and trifluoroacetic acid.

It was then possible to make use of a table given in the International Critical Tables (12), in which are presented the values of the functions $g\rho r^2/\gamma$, and V_m/r^3 , where g is the gravity constant (980.7 cm./sec.²), ρ is the liquid density (gm./cc.), r is the radius of the tube (cm.), γ is the surface tension (dynes/cm.), and V_m is the volume of the meniscus (cc.). If g , ρ , r , and γ are known, it is possible to calculate V_m .

From the available surface tension data for acetic acid and trichloroacetic acid, the approximate values for the surface tension of trifluoroacetic acid were obtained. These values are presented in Table 8. The liquid density and the tube radius are known; therefore, $g\rho r^2/\gamma$ may be calculated, from which V_m may be obtained. These results for trifluoroacetic acid are presented in Table 8. They are graphically depicted in Figure 15, in which the meniscus volume is plotted as a function of temperature.

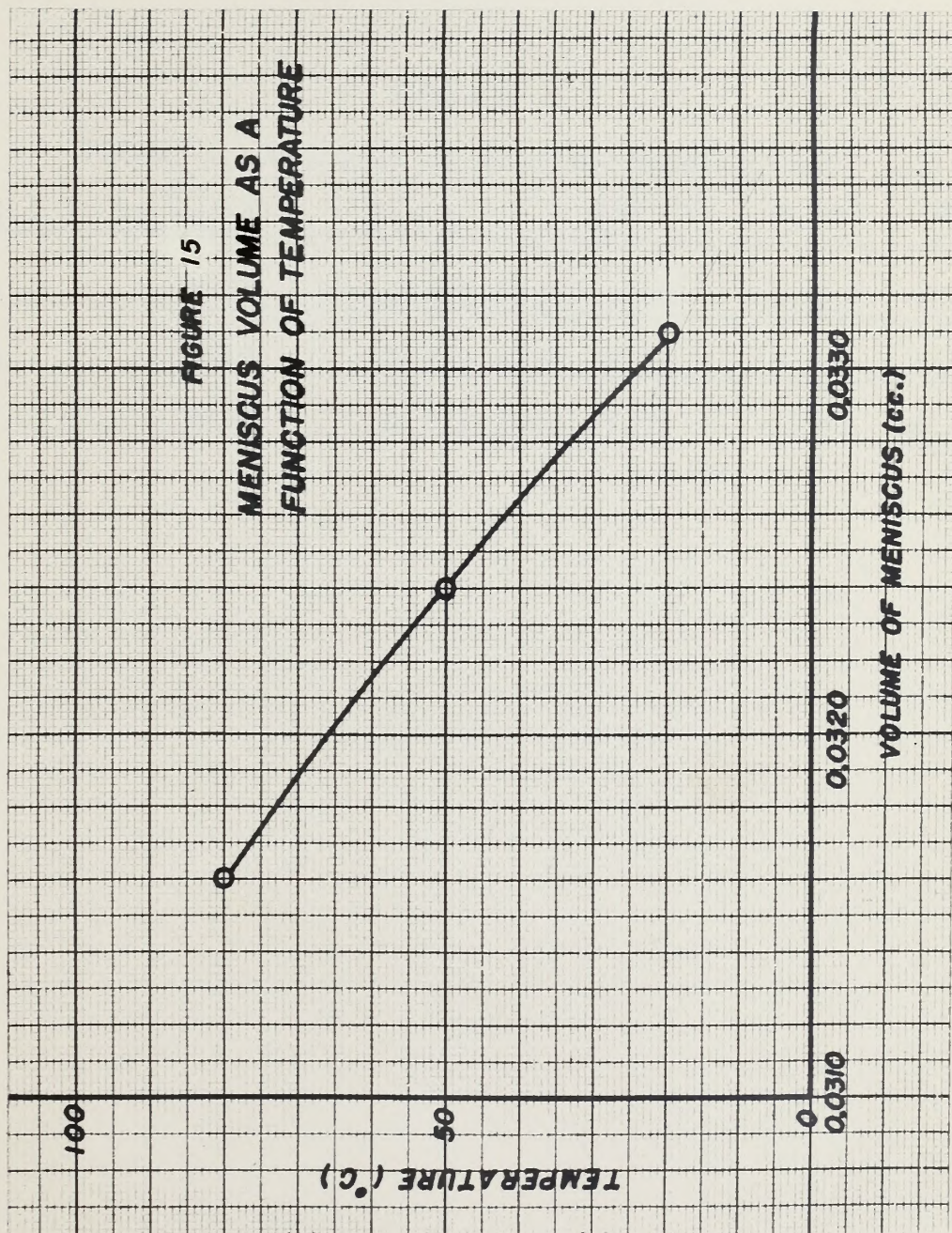
If one assumes that the meniscus volume as calculated by this procedure is in error by 50%, use of these values of the meniscus volume introduces a maximum error of 0.3% into the determination of the liquid volume in the burette in the

their respective surface tensions at comparable temperatures do not differ by more than 80%. The third assumption necessary is that $d\gamma/dT$ (where γ represents the surface tension) is the same for acetic acid, trichloroacetic acid, and trifluoroacetic acid.

It was then possible to make use of a table given in the International Critical Tables (12), in which are presented the values of the functions $g/r^{2/3}$, and $V_m^{2/3}$, where g is the gravity constant (980.7 cm./sec.²), ρ is the liquid density (gm./cc.), r is the radius of the tube (cm.), γ is the surface tension (dynes/cm.), and V_m is the volume of the meniscus (cc.). If g , r , and γ are known, it is possible to calculate V_m .

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If one assumes that the meniscus volume as calculated by this procedure is in error by 50%, use of these values of the meniscus volume introduces a maximum error of 0.5% into the determination of the liquid volume in the burette in the



vapor density calculations (see below). In all probability, the error is not that large.

Table 8

Volume of Meniscus of Trifluoroacetic Acid						
t (C.)	γ dynes/cm.	r (cm.)	gpr^2/γ	V_m/r^3	V_m	
20	33.2	0.2	1.4902	7.04	0.517	0.0331
50	30.3	0.2	1.4154	7.33	0.507	0.0324
80	27.3	0.2	1.3409	7.71	0.494	0.0316

Determination of the Vapor Density of Trifluoroacetic Acid.

A description of the bulb-and-burette assembly has already been presented in Section II.

The burette, as received, was simply a tube of assumedly uniform bore, open at both ends. It was cleaned and calibrated for uniformity of bore with both ends open. To clean the burette tube, it was immersed in aqua regia for six hours, washed with two liters of distilled water, then soaked in cleaning solution overnight, and finally washed with five liters of distilled water. It was then rinsed with successive portions of acetone and ether, and sucked dry on the house vacuum.

The procedure used for calibrating the tube for uniformity of bore was identical with that already described for the dilatometer capillary. The results of this calibration are presented in Table 30 (Appendix 1). The tube was found to be essentially uniform (± 0.001 mm).

A reference scratch was marked at one end of the tube with a diamond tool. The other end was sealed shut. Then the burette was weighed, filled with distilled water to a point above the reference mark, and mounted by means of a collar in a tube through which water was circulated by a small circulating pump. The water source was a thermostated bath, controlled to $\pm 0.04^{\circ}$ C. The entire water column in

Determination of the Vapor Density of Trifluoroacetic Acid.

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the burette was submerged in the circulating water. By suitable adjustment of the wire collar, the tube was aligned to the vertical against the crosshair of the cathetometer telescope and the heights of the reference scratch and the meniscus were determined. The burette was then dried and weighed, after which it was emptied and refilled about half full with water. The walls of the burette above the liquid level were dried by repeated warming of the burette with a smoky flame. The burette was then mounted in the thermostat, aligned to the vertical, and the heights of the reference scratch and the meniscus were read with the cathetometer. In both sets of readings, the usual precautions were taken to check the precision of the observer. These data are given in Table 31 (Appendix 1), along with the volume of the burette (expressed in cc./cm. of tube length, and in cc. to the reference mark).

The bulb was cleaned in a similar fashion, and thoroughly washed. It was filled with distilled water to a reference mark on a short length of capillary sealed to the bulb, and immersed in the water bath. The bulb was permitted to come to equilibrium with its surroundings, the level of the meniscus in the capillary was adjusted to coincide with the mark, and the bulb was weighed. It was emptied, dried by heating while under vacuum, cooled, and weighed again. The results are recorded in Table 32 (Appendix 1), along with the volume of the bulb to the mark as calculated from these data.

the burette was submerged in the circulating water. By slight adjustment of the wire collar, the tube was aligned to the vertical against the crosshair of the cathetometer telescope and the heights of the reference scratch and the meniscus were determined. The burette was then dried and weighed, after which it was emptied and refilled about half full with water. The walls of the burette above the liquid level were dried by repeated warming of the burette with a smoky flame. The burette was then mounted in the thermostat, aligned to the vertical, and the heights of the reference scratch and the meniscus were read with the cathetometer. In both sets of readings, the usual precautions were taken to check the precision of the observer. These data are given in Table 31 (Appendix I), along with the volume of the burette (expressed in cc./cm. of tube length, and in cc. to the reference mark).

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The connecting arm (Figure 8) was made by bending a length of 3 mm. capillary tubing to the proper size. The filling nipple was sealed on, and the whole arm was annealed. Then it was cleaned, washed and dried. It was filled with mercury and the mercury was weighed. These data are recorded in Table 33 (Appendix 1), along with the volume of the connecting arm obtained from these measurements.

The connecting arm was wrapped, and the bulb-and-burette assembly was blown together. The latter was attached to a manifold through the filling nipple. A storage bulb was fitted with a ground glass male joint; it was wiped clean, weighed,^{*} and attached to the manifold through its female couple. Only the lower half of the joint was greased, to reduce the possibility of contamination of the acid. The manifold was also equipped with a manometer. The assembly was connected to the high vacuum line through a stopcock, and the system was evacuated. During the pumping process, the bulb-and-burette assembly was degassed by heating. The apparatus was tested at intervals and was regarded as having reached a satisfactory state of evacuation when the pressure rose from $< 10^{-5}$ to 5×10^{-5} mm. in two hours. The stopcock was then closed, the arms of the manometer were read and the breakoff

^{*} Since it was realized that there might be some difficulty in quantitative cleaning of the storage bulb after being greased and extensively handled, several weighings were made on a joint, duplicating the procedure used above. It was found possible to check a weighing to ± 0.0001 gm. consistently.

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tip was smashed. The acid sample in the storage bulb was distilled into the burette; the distillation was considered complete when the mercury in the arms of the manometer returned to its original position. The bulb and burette were then chilled to dry ice temperature, the system was opened to the high vacuum line, and the bulb-and-burette assembly was sealed off. The storage bulb was removed, wiped clean, and weighed. The weighing data are recorded in Table 34. (Appendix 1).

The bulb-and-burette assembly was mounted in the thermostats through holes cut in the lids for the purpose by means of claw clamps fixed to the sides of the thermostats. The heater was connected through a "powerstat" to the line, and the connecting arm was heated slowly to operating temperature ($>160^{\circ}$ C.). Thermostat "B" was set at a given temperature and held at that temperature throughout a run. Thermostat "A" was set at some temperature higher than that of thermostat "B" and readings on the liquid level in the burette were taken with the cathetometer. Then Thermostat "A" was raised about 10° and the liquid level was read again. The data so obtained are presented in Tables 35-41 (Appendix 1). The first two columns record the time of the reading (considering the beginning of a run, or the beginning of a day's operations, as zero time), the third and fourth columns show the degree of balance of the potentiometer circuit (the circuit was balanced before each reading). The next three columns

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high vacuum line, and the bulb-and-burette assembly was
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weighed. The weighing data are recorded in Table 34.

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The bulb-and-burette assembly was mounted in the
thermostat through holes cut in the lids for the purpose by
means of claw clamps fixed to the sides of the thermostat.
The heater was connected through a "powerstat" to the line,
and the connecting arm was heated slowly to operating temper-
ture ($> 150^{\circ}\text{C.}$). Thermostat "B" was set at a given temper-
ture and held at that temperature throughout a run. Thermo-
stat "A" was set at some temperature higher than that of
thermostat "B" and readings on the liquid level in the burette
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sidering the beginning of a run, or the beginning of a day's
operations, as zero time), the third and fourth columns show
the degree of balance of the potentiometer circuit (the circuit
was balanced before each reading). The next three columns

record the potentiometer setting (in $\mu\text{v.}$), the galvanometer reading, and the temperature of thermostat "A" calculated from these data. The eighth, ninth, and tenth columns present the corresponding data for thermostat "B". The next column records the temperature of the connecting arm, and the last column shows the height of the liquid level and the reference scratch as observed with the cathetometer. The height of the reference mark was noted at the beginning and end of the readings taken at each temperature setting of thermostat "A". At least three readings were taken of the height of the liquid level at each setting of the bulb thermostat. The usual precautions were observed to ensure temperature equilibrium.

The density of the liquid at temperature T_1

ρ = the density of the vapor at temperature T_1

V = the volume of the vapor in the burette at temperature T_1

w = the mass of the vapor in the connecting arm at temperature T_1

w_b = the mass of the vapor in the burette at temperature T_1

Then

$$V_1\rho + V_v d = \mu \quad (1)$$

where μ is the mass of the sample corrected for the vapor in the connecting tube between bulb and burette and for the vapor in the burette itself.

If ρ is known at the temperature T_1 , and V_1 , V_v , and μ are known, equation (1) can be solved for the vapor

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reading, and the temperature of thermostat "A" calculated
from these data. The eighth, ninth, and tenth columns
present the corresponding data for thermostat "B". The next
column records the temperature of the connecting arm, and the
last column shows the height of the lipid level and the
reference scratch as observed with the cathetometer. The
height of the reference mark was noted at the beginning and
end of the readings taken at each temperature setting of
thermostat "A". At least three readings were taken of the
height of the lipid level at each setting of the bulb thermo-
stat. The usual precautions were observed to ensure tempera-
ture equilibrium.

Method of Analysis of the Data.

Let:

m = the total mass of the sample (m selected greater than the mass of the saturated vapor that will fill the system)

T_1 = the temperature of the burette

T_v = the temperature of the bulb (T_v T_1)

T_a = the temperature of the connecting arm
(T_a T_v , T_1)

V_1 = the volume of the liquid in the burette

V_v = the volume of the bulb

V_a = the volume of the connecting arm

ρ = the density of the liquid at temperature T_1

d = the density of the vapor at temperature T_v

V_b = the volume of the vapor in the burette at temperature T_1

w_a = the mass of the vapor in the connecting arm at temperature T_a

w_b = the mass of the vapor in the burette at temperature T_b

Then

$$V_1\rho + V_v d = \mu \quad (1)$$

where μ is the mass of the sample corrected for the vapor in the connecting tube between bulb and burette and for the vapor in the burette itself.

If ρ is known at the temperature T_1 , and V_1 , V_v , and μ are known, equation (1) can be solved for the vapor

Method of Analysis of the Data.

Let:

m = the total mass of the sample (a selected greater than the mass of the saturated vapor that will fill the system)

T_l = the temperature of the burette

T_v = the temperature of the bulb ($T_v = T_l$)

T_s = the temperature of the connecting arm ($T_s = T_l, T_v$)

V_l = the volume of the liquid in the burette

V_v = the volume of the bulb

V_s = the volume of the connecting arm

ρ_l = the density of the liquid at temperature T_l

ρ_v = the density of the vapor at temperature T_v

V_d = the volume of the vapor in the burette at temperature T_l

w_s = the mass of the vapor in the connecting arm at temperature T_s

w_b = the mass of the vapor in the burette at temperature T_b

Then

$$(1) \quad V_l \rho_l + V_d \rho_v = m$$

where m is the mass of the sample corrected for the vapor in the connecting tube between bulb and burette and for the vapor in the burette itself.

If ρ is known at the temperature T_l , and V_l, V_v , and V_s are known, equation (1) can be solved for the vapor

density d ; it will be the vapor density at the temperature T_v and at a pressure equal to the vapor pressure of the liquid at temperature T_1 .

V_v can be obtained by any of the usual methods for calibration of a bulb; V_1 can be obtained by calibration of the burette in terms of volume per unit length, and the reading off of the liquid height by means of a cathetometer; ρ , the liquid density, must be determined independently (for details of these measurements, see below).

The problem of calculating d devolves, then, into the determination of μ . To determine μ , one must evaluate the mass of vapor in the connecting arm and in the burette above the liquid level. This can be readily seen when expressed mathematically:

$$\begin{aligned} \mu &= m - w_a - w_b \\ \text{or,} \quad \mu &= m - V_a d_a - V_b d_b \end{aligned} \quad (2)$$

where d_a is the density of the vapor at temperature T_a and d_b is the density of the vapor at the temperature T_1 . The problem of evaluating μ then becomes the question of the appropriate values to be assigned to d_a and d_b .

Let us rewrite equation (1), employing our new definition of μ . It becomes

$$\begin{aligned} V_1 \rho + V_v d &= m - V_a d_a - V_b d_b \\ \text{or,} \quad d &= \frac{m - V_1 \rho - V_a d_a - V_b d_b}{V_v} \end{aligned} \quad (3)$$

density δ ; it will be the vapor density at the temperature T and at a pressure equal to the vapor pressure of the liquid at temperature T_1 .

V_v can be obtained by any of the usual methods for calibration of a bulb; V_1 can be obtained by calibration of the burette in terms of volume per unit length, and the reading off of the liquid height by means of a cathetometer; ρ , the liquid density, must be determined independently (for details of these measurements, see below).

The problem of calculating δ involves, then, into the determination of μ . To determine μ , one must evaluate the mass of vapor in the connecting arm and in the burette above the liquid level. This can be readily seen when expressed mathematically:

$$\begin{aligned} \mu &= m - w_a - w_b \\ \mu &= m - V_a \delta_a - V_b \delta_b \end{aligned} \quad \text{or,} \quad (2)$$

where δ_a is the density of the vapor at temperature T_a and δ_b is the density of the vapor at the temperature T_1 . The problem of evaluating μ then becomes the question of the appropriate values to be assigned to δ_a and δ_b .

Let us rewrite equation (1), employing our new defi-

nition of μ . It becomes

$$\begin{aligned} V_1 \rho + V_v \delta = m - V_a \delta_a - V_b \delta_b \\ \delta = \frac{m - V_1 \rho - V_a \delta_a - V_b \delta_b}{V_v} \end{aligned} \quad \text{or,} \quad (3)$$

Clearly d_a and d_b can not be evaluated directly since we have one equation and three unknowns. They may, however, be evaluated with sufficient precision by use of an approximation method as described below.

The data are obtained by setting the thermostat containing the burette at a fixed temperature and raising the temperature of the thermostat containing the bulb to successively higher temperatures. At the beginning of a run, $T_v (= T_{v2})$ is not much greater than T_1 ; at the end of a run, $T_v (= T_{v1})$ is not much less than T_a .

As a first approximation, we may assume that Charles' Law applies, and that, therefore, we may correct the volume of vapor in the arm at T_a to the volume which it would occupy at T_{v1} ; similarly, we may correct the volume of vapor in the burette at T_1 to the volume which it would occupy at T_{v1} . Thus,

$$\rho^{d(T_{v1})}_1 = \frac{m - V_1 \rho}{V_v + V_a(T_{v1}/T_a) + V_b(T_{v1}/T_1)} \quad (4)$$

Likewise, we may correct the volume of vapor in the arm at T_a to the volume which it would occupy at T_{v2} ; and we may correct

* N. E. This notation is to be read "the density of the vapor at temperature T_{v1} ; first approximation."

Clearly d_a and d_p can not be evaluated directly since we have one equation and three unknowns. They may, however, be evaluated with sufficient precision by use of an approximation method as described below.

The data are obtained by setting the thermostat containing the burette at a fixed temperature and raising the temperature of the thermostat containing the bulb to successively higher temperatures. At the beginning of a run, T_v (= T_{v_s}) is not much greater than T_i ; at the end of a run, T_v (= T_{v_f}) is not much less than T_a .

As a first approximation, we may assume that Charles' law applies, and that, therefore, we may correct the volume of vapor in the arm at T_a to the volume which it would occupy at T_{v_i} ; similarly, we may correct the volume of vapor in the burette at T_i to the volume which it would occupy at T_{v_i} . Thus,

$$(A) \quad \frac{m - V_i^v}{V_v + V_a(T_{v_i}/T_a) + V_b(T_{v_i}/T_i)} = \frac{\Delta(T_{v_i})}{\Delta(T_{v_i})}$$

Likewise, we may correct the volume of vapor in the arm at T_a to the volume which it would occupy at T_{v_s} ; and we may correct

* N. E. This notation is to be read "the density of the vapor at temperature T_i : first approximation."

the volume of vapor in the burette at T_1 to the volume which it would occupy at T_{v2} . Thus

$$\Delta^{d(T_{v2})}_1 = \frac{m - V_1 \rho}{V_v + V_a(T_{v2}/T_a) + V_b(T_{v2}/T_1)} \quad (5)$$

We may now refine these values of $d(T_{v1})$ and $d(T_{v2})$ by substituting these terms for d_a and d_b , successively, in equation (3) and, still assuming that Charles' Law applies, we obtain the equations

$$\Delta^{d(T_{v1})}_2 = \frac{m - V_1 \rho - V_a(T_{v1}/T_a) \Delta^{d(T_{v1})}_1 - V_b(T_{v1}/T_1) \Delta^{d(T_{v2})}_1}{V_v} \quad (6)$$

$$\Delta^{d(T_{v2})}_2 = \frac{m - V_1 \rho - V_a(T_{v2}/T_a) \Delta^{d(T_{v1})}_1 - V_b(T_{v2}/T_1) \Delta^{d(T_{v2})}_1}{V_v}$$

Solving for $\Delta^{d(T_{v1})}_2$ and $\Delta^{d(T_{v2})}_2$, we obtain more refined values of $d(T_{v1})$ and $d(T_{v2})$. Then substituting these new values in equations (6) we may obtain still more refined values of $d(T_{v1})$ and $d(T_{v2})$. This process is continued until two successive values of $d(T_{v1})$ and $d(T_{v2})$, respectively, are obtained which are constant. The assumption is now made that $\Delta^{d(T_{v1})}_n = d_a$ and that $\Delta^{d(T_{v2})}_n = d_b$. These values may then be substituted into equation (3) and we obtain

$$d = \frac{m - V_1 \rho - V_a \Delta^{d(T_{v1})}_n - V_b \Delta^{d(T_{v2})}_n}{V_v} \quad (8)$$

and equation (8) may be solved for d at various temperatures.

the volume of vapor in the barometer at T_1 to the volume which

it would occupy at T_{vS} . Thus

$$(2) \quad \frac{m - v_{I1}}{v + v_a(T_{vS}/T_1) + v_b(T_{vS}/T_1)} = \frac{v_{vI}^d(T_{vS})}{v_{vI}^d(T_1)}$$

We may now refine these values of $v_{vI}^d(T_1)$ and $v_{vI}^d(T_{vS})$ by substituting these terms for v_a and v_b , successively, in equation (2) and, still assuming that Charles' law applies, we obtain

the equations

$$\frac{v_{vI}^d(T_{vS})}{v_{vI}^d(T_1)} = \frac{m - v_{I1} - v_a(T_{vI}^d(T_{vS})/T_1) - v_b(T_{vI}^d(T_{vS})/T_1)}{v + v_a(T_{vI}^d(T_{vS})/T_1) + v_b(T_{vI}^d(T_{vS})/T_1)}$$

$$\frac{v_{vI}^d(T_{vS})}{v_{vI}^d(T_1)} = \frac{m - v_{I1} - v_a(T_{vI}^d(T_{vS})/T_1) - v_b(T_{vI}^d(T_{vS})/T_1)}{v + v_a(T_{vI}^d(T_{vS})/T_1) + v_b(T_{vI}^d(T_{vS})/T_1)}$$

Solving for $v_{vI}^d(T_{vS})$ and $v_{vI}^d(T_1)$, we obtain more refined values of $v_{vI}^d(T_{vS})$ and $v_{vI}^d(T_1)$. Then substituting these new values in equations (2) we may obtain still more refined values of $v_{vI}^d(T_{vS})$ and $v_{vI}^d(T_1)$. This process is continued until two successive values of $v_{vI}^d(T_{vS})$ and $v_{vI}^d(T_1)$, respectively, are obtained which are constant. The assumption is now made

that $v_{vI}^d(T_{vS}) = v_a$ and that $v_{vI}^d(T_1) = v_b$. These values may then be substituted into equation (2) and we obtain

$$(3) \quad \frac{m - v_{I1} - v_a(T_{vI}^d(T_{vS})/T_1) - v_b(T_{vI}^d(T_{vS})/T_1)}{v + v_a(T_{vI}^d(T_{vS})/T_1) + v_b(T_{vI}^d(T_{vS})/T_1)} = \frac{v_{vI}^d(T_{vS})}{v_{vI}^d(T_1)}$$

and equation (3) may be solved for d at various temperatures.

V_1 must be corrected for the meniscal height in the burette and for the thermal expansion of the burette. The latter correction is quite simply made. Let us assume that the volume of the burette (expressed in cc. or $\frac{1}{n}$ cc/cm.) is known at some temperature t_0 . Let this volume be V_0 . The coefficient of cubical expansion of glass is g . Then, the volume V_t at any other temperature t may be found by use of the expression

$$V_t = V_0 [1 + (t - t_0)g]$$

The meniscus correction has already been discussed.

The vapor density, d , which has been calculated by means of equation (8), may now be used to calculate the apparent molecular weight of the vapor, M_v by the assumption of the perfect gas law:

$$M_v = \frac{dRT_v}{P}$$

This is the value of the molecular weight of the vapor at the vapor pressure of the liquid and at the temperature of the bulb. It will be recalled that data are obtained by holding T_1 constant and raising T_v to successively higher temperatures. Thus, the data are experimentally recorded as a series of isobars. It is, however, more instructive to consider these data as isotherms and therefore the family of isobaric curves is crossread at convenient temperatures and plotted, showing the variation of molecular weight with pressure for various temperatures.

V must be corrected for the meniscus height in the burette and for the thermal expansion of the burette. The latter correction is quite simply made. Let us assume that the volume of the burette (expressed in cc. or $\frac{1}{1000}$ m.) is known at some temperature t_0 . Let this volume be V_0 . The coefficient of cubical expansion of glass is α . Then, the volume V_t at any other temperature t may be found by use of the expression

$$V_t = V_0 [1 + (t - t_0)\alpha]$$

The meniscus correction has already been discussed. The vapor density, d , which has been calculated by means of equation (2), may now be used to calculate the apparent molecular weight of the vapor, M_v , by the assumption of the perfect gas law:

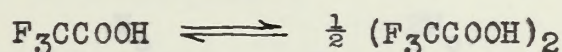
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If one assumes that trifluoroacetic acid vapor exists as a mixture of monomer and dimer in dynamic equilibrium, the total pressure, P , may be defined as

$$P = p_1 + p_2 \quad (9)$$

where p_1 = the partial pressure of trifluoroacetic acid monomer, and p_2 = the partial pressure of trifluoroacetic acid dimer. The equilibrium may be represented as



and the equilibrium constant K_d is defined by the relationship

$$K_d = \frac{p_2}{p_1^2} \quad ; \quad \text{or} \quad p_2 = K_d p_1^2$$

If this expression is substituted in equation (9), one obtains

$$P = p_1 + K_d p_1^2$$

and, dividing by P ,

$$1 = \frac{p_1}{P} + K_d \frac{p_1^2}{P} \quad (10)$$

Let X_1 be the mole fraction of monomer. Then $X_1 = \frac{p_1}{P}$ and equation (10) becomes

$$X_1 + K_d X_1^2 P = 1$$

or, since $p_1 = X_1 P$,

$$X_1 + K_d X_1^2 P = 1 \quad (11)$$

If one considers that of every mole of monomer, β mole associates to form $(\beta/2)$ mole of dimer, then, obviously, the mixture will contain $(1 - \beta)$ mole of monomer,

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$$X_1 + K_d X_1^2 P = 1$$

or, since $p_1 = X_1 P$,

$$(11) \quad X_1 + K_d X_1^2 P = 1$$

If one considers that of every mole of monomer, 3 mole associated to form $(\frac{3}{2})$ mole of dimer, then, obviously, the mixture will contain $(1 - \frac{3}{2}X_1)$ mole of monomer,

$(\beta/2)$ mole of dimer, and therefore $(1 - [\beta/2])$ mole total. Therefore, X_1 , the mole fraction of monomer, may be expressed as

$$X_1 = \frac{1 - \beta}{1 - (\beta/2)} = \frac{2(1 - \beta)}{2 - \beta} \quad (12)$$

Also, the apparent molecular weight of the vapor, which is defined as the mass of the vapor divided by the number of moles is

$$M_v = \frac{M_o}{1 - \beta/2} = \frac{2M_o}{2 - \beta} \quad (13)$$

Expressing X_1 in terms of M_v and M_o , one obtains

$$X_1 = \frac{2M_o - M_v}{M_o} \quad (14)$$

and, substituting this value for X_1 into equation (11), K_d^2 is obtained as

$$K_d^2 = \frac{M_o(M_v - M_o)}{(2M_o - M_v)^2 P} \quad (15)$$

From the coordinated values of P and M_v obtainable from the series of isotherms derived above, K_d may be calculated. The values for K_d are found not to be constant for a given temperature; they do, however, approach a limiting value as the pressure increases. After consideration (cf. Sections IX and X) it was concluded that the tendency toward polymerization stops with the dimer in trifluoroacetic acid and therefore, that further analysis was superfluous.

(2/2) mole of dimer, and therefore (1 - [2/2]) mole total. Therefore, X_1 , the mole fraction of monomer, may be expressed as

$$(12) \quad X_1 = \frac{1 - \frac{2}{2}}{1 - \frac{2}{2}} = \frac{2(1 - \frac{2}{2})}{2 - 2}$$

Also, the apparent molecular weight of the vapor, which is defined as the mass of the vapor divided by the number of moles is

$$(13) \quad M_v = \frac{M_o}{1 - \frac{2}{2}} = \frac{2M_o}{2 - 2}$$

Expressing X_1 in terms of M_v and M_o , one obtains

$$(14) \quad X_1 = \frac{2M_o - M_v}{M_o}$$

and, substituting this value for X_1 into equation (11), K_d

is obtained as

$$(15) \quad \frac{2}{K_d} = \frac{M_o(M_v - M_o)}{(2M_o - M_v)^2}$$

From the coordinated values of P and M_v obtainable from the series of isotherms derived above, K_d may be calculated. The values for K_d are found not to be constant for a given temperature; they do, however, approach a limiting value as the pressure increases. After consideration (cf. Sections IX and X) it was concluded that the tendency toward polymerization stops with the dimer in trifluoroacetic acid and therefore, that further analysis was superfluous.

Calculation of the Vapor Density.

The theoretical development of the method used to evaluate the vapor density has already been fully discussed. It is felt that it might be advantageous to illustrate this procedure with a typical example and Point 4 of Run 3 has been selected for this purpose.

The temperature of thermostat "B" (= the temperature of the liquid acid = the temperature of the vapor in the burette) (T_1 or T_b) = 50.76° C.

The temperature of the connecting arm (= the temperature of the acid vapor in the arm) (T_a) = 168° C.

The total mass of the sample (m) = 3.0868 gm.

The temperature of thermostat "A" (= the temperature of the acid vapor in the bulb) (T_v) = 97.08° C.

.....
The liquid density (ρ):

$$\begin{aligned}\rho &= 1.5402 - (2.506 \times 10^{-3})t + (1.863 \times 10^{-7})t^2 \\ &= 1.5402 - (2.506 \times 10^{-3})(50.76) + (1.863 \times 10^{-7})(50.76)^2 \\ &= 1.5402 - 0.1272 + 0.0005 \\ &= 1.4135 \text{ gm./cc.}\end{aligned}$$

The volume of liquid in the burette (V_1):

the volume of the burette to the reference mark
at 24.82° C. = 2.9845 cc.

the volume of the burette to the reference mark at
50.76° C. = 2.9845 $\left[1 + (50.76 - 24.82)(25 \times 10^{-6}) \right]$
= 2.9864 cc.

Calculation of the Vapor Density.

The theoretical development of the method used to evaluate the vapor density has already been fully discussed. It is felt that it might be advantageous to illustrate this procedure with a typical example and point 4 of Run 3 has been selected for this purpose.

The temperature of thermostat "B" (T_B) = the temperature of the liquid acid = the temperature of the vapor in the burette (T_1 or T_2) = 80.75° C.

The temperature of the connecting arm (T_c) = the temperature of the acid vapor in the arm (T_3) = 168° C.

The total mass of the sample (m) = 3.0888 gm.

The temperature of thermostat "A" (T_A) = the temperature of the acid vapor in the bulb (T_4) = 97.08° C.

.....

The liquid density (ρ):

$$\begin{aligned} \rho &= 1.5402 - (2.50 \times 10^{-3}) + (1.86 \times 10^{-7}) t^2 \\ &= 1.5402 - (2.50 \times 10^{-3}) (80.75) + (1.86 \times 10^{-7}) (80.75)^2 \\ &= 1.5402 - 0.1278 + 0.0005 \\ &= 1.4135 \text{ gm./cc.} \end{aligned}$$

The volume of liquid in the burette (V_1):

$$\begin{aligned} \text{the volume of the burette to the reference mark at } 24.82^\circ \text{ C.} &= 2.9845 \text{ cc.} \\ \text{the volume of the burette to the reference mark at } 80.75^\circ \text{ C.} &= 2.9845 [1 + (50.75 - 24.82)(25 \times 10^{-6})] \\ &= 2.9864 \text{ cc.} \end{aligned}$$

the volume of the burette expressed in cc./cm.
at 25.65° C. = 5.0803×10^{-2} cc./cm.

the volume of the burette expressed in cc./cm.
at 50.76° C. = $5.0803 \times 10^{-2} \left[1 + (50.76 - 25.65)(25 \times 10^{-6}) \right]$
= 5.0835×10^{-2}

the distance from the meniscus to the reference mark
= 56.148 - 31.260
= 24.888 cm.

~~The volume of the liquid in the burette (V_1) (uncorrected):~~

$$V_1 \text{ (uncorrected)} = 2.9864 - (24.888)(5.0835 \times 10^{-2})$$

$$= 1.7212 \text{ cc.}$$

at 50.76° C., the volume of the meniscus = 0.0324 cc.

$$V_1 \text{ (corrected)} = 1.7212 + 0.0324$$

$$= 1.7536 \text{ cc.}$$

The volume of vapor in the burette (V_b):

$$V_b \text{ (uncorrected)} = (24.888)(5.0835 \times 10^{-2})$$

$$= 1.2652 \text{ cc.}$$

$$V_b \text{ (corrected)} = 1.2652 - 0.0324$$

$$= 1.2328 \text{ cc.}$$

The volume of vapor in the bulb (V_v):

the volume of the bulb at 25.67° C. = 253.274 cc.

$$V_v = 253.274 \left[1 + (97.08 - 25.67)(25 \times 10^{-6}) \right]$$

$$= 253.730 \text{ cc.}$$

The volume of vapor in the connecting arm (V_a):

the volume of the connecting arm at 22.2° C. = 5.261 cc.

$$V_a = 5.261 \left[1 + (168.0 - 22.2)(25 \times 10^{-6}) \right]$$

$$= 5.280 \text{ cc.}$$

the volume of the burette expressed in cc./cm.
at 25.50° C. = 5.0803×10^{-8} cc./cm.

the volume of the burette expressed in cc./cm.
at 50.76° C. = $5.0803 \times 10^{-8} [1 + (50.76 - 25.50)(2.5 \times 10^{-5})]$

$$= 5.0835 \times 10^{-8}$$

the distance from the meniscus to the reference mark

$$= 55.148 - 31.860$$

$$= 24.888 \text{ cm.}$$

~~The volume of the liquid in the burette (V_l) is:~~

$$V_l \text{ (uncorrected)} = 2.9864 - (24.888)(5.0835 \times 10^{-8})$$

$$= 1.7312 \text{ cc.}$$

at 50.76° C., the volume of the meniscus = 0.0324 cc.

$$V_l \text{ (corrected)} = 1.7312 + 0.0324$$

$$= 1.7636 \text{ cc.}$$

The volume of vapor in the burette (V_b):

$$V_b \text{ (uncorrected)} = (24.888)(5.0835 \times 10^{-8})$$

$$= 1.2652 \text{ cc.}$$

$$V_b \text{ (corrected)} = 1.2652 - 0.0324$$

$$= 1.2328 \text{ cc.}$$

The volume of vapor in the bulb (V_v):

the volume of the bulb at 25.57° C. = 252.274 cc.

$$V_v = 252.274 [1 + (27.08 - 25.57)(2.5 \times 10^{-5})]$$

$$= 252.730 \text{ cc.}$$

The volume of vapor in the connecting arm (V_a):

the volume of the connecting arm at 22.2° C. = 5.281 cc.

$$V_a = 5.281 [1 + (168.0 - 22.2)(2.5 \times 10^{-5})]$$

$$= 5.280 \text{ cc.}$$

When these data have been calculated for all points in a run, it is possible to employ the approximation method outlined in Section VIII. Using Points 1 and 9 of Run 3, the data, as evaluated by the operations just described, are found to be:

	Point 1	Point 9
m	3.0868 gm.	3.0868 gm.
V_1	1.6192 cc.	1.8930 cc.
ρ	1.4135 gm./cc.	1.4135 gm./cc.
V_v	253.527 cc.	254.069 cc.
V_a	5.280 cc.	5.280 cc.
V_b	1.3672 cc.	1.0934 cc.
$T_{v1} (-T_v)$		151.35° C. (424.51° K.)
$T_{v2} (-T_v)$	65.63° C. (338.79° K.)	
T_a	168° C. (441.16° K.)	168° C. (441.16° K.)
T_1	50.76° C. (323.92° K.)	50.76° C. (323.92° K.)

Making use of Equation (4) of Section VIII,

$$\frac{d(T_{v1})}{dz}_1 = \frac{3.0868 - (1.8930)(1.4135)}{254.069 + (5.280)(424.51/441.16) + (1.0934)(424.51/323.92)}$$

$$= 1.5773 \times 10^{-3} \text{ gm./cc.}$$

Substituting in Equation (5) of Section VIII,

$$\frac{d(T_{v2})}{dz}_1 = \frac{3.0868 - (1.6192)(1.4135)}{253.527 + (5.280)(338.79/441.16) + (1.3672)(33.879/323.92)}$$

$$= 3.0814 \times 10^{-3} \text{ gm./cc.}$$

When these data have been calculated for all points in a run, it is possible to employ the approximation method outlined in Section VIII. Using Points 1 and 2 of Run 1, the data, as evaluated by the operations just described, are found to be:

	Point 1	Point 2
m	3.0868 gm.	3.0868 gm.
V ₁	1.6182 cc.	1.6930 cc.
P	1.4135 gm./cc.	1.4135 gm./cc.
V _v	233.327 cc.	234.089 cc.
V _a	2.280 cc.	2.280 cc.
V _d	1.3672 cc.	1.0934 cc.
T _{v1} (°C.)	55.63°	51.38°
T _{v1} (°K.)	(328.79° K.)	(424.51° K.)
T _a	168° C.	168° C.
T _a	(441.15° K.)	(441.15° K.)
T _l	50.76° C.	50.76° C.
T _l	(323.92° K.)	(323.92° K.)

Making use of Equation (4) of Section VIII,

$$\frac{1}{T_{v1}} = \frac{234.089 + (2.280)(441.15) + (1.0934)(424.51)}{323.92} = 1.5775 \times 10^{-3} \text{ gm./cc.}$$

Substituting in Equation (5) of Section VIII,

$$\frac{1}{T_{v2}} = \frac{233.327 + (2.280)(328.79/441.15) + (1.3672)(32.879/323.92)}{323.92} = 3.0614 \times 10^{-3} \text{ gm./cc.}$$

Substituting in Equations (6), we obtain,

$$d_{(T_{v1})_2} = \frac{3.0868 - (1.8930)(1.4135) - (5.280)(424.51/441.16)}{(1.5773 \times 10^{-3}) - (1.0934)(424.51/323.92)(3.0814 \times 10^{-3})} \\ 254.069$$

$$d_{(T_{v2})_2} = \frac{3.0868 - (1.6192)(1.4135) - (5.280)(338.79/441.16)}{(1.5773 \times 10^{-3}) - (1.3672)(338.79/323.92)(3.0814 \times 10^{-3})} \\ 253.527$$

from which we obtain that

$$d_{(T_{v1})_2} = 1.5688 \times 10^{-3} \text{ gm./cc.}$$

$$\text{and } d_{(T_{v2})_2} = 3.1054 \times 10^{-3} \text{ gm./cc.}$$

Resubstituting these new values for the vapor density into equations (6) and solving

$$d_{(T_{v1})_3} = 1.5688 \times 10^{-3} \text{ gm./cc.}$$

$$d_{(T_{v2})_3} = 3.1054 \times 10^{-3} \text{ gm./cc.}$$

Operating on the assumption that the vapor density at $151.35^\circ \approx$ the vapor density at 168° and, similarly, that the vapor density at $65.63^\circ \approx$ the vapor density at 50.76° , it is possible to calculate the density of trifluoroacetic acid vapor at each setting of thermostat "A". Such an assumption introduces an error of approximately 4.2% into the calculation of the factors $V_a d_a$ and $V_b d_b$ (Equation 3 of Section VIII). This, however, leads to an error of only 0.02% in the calculation of the vapor density, d_v , at the temperature T_v , inasmuch as these two factors are only a small percentage of the total volume of vapor. Using Point 4 of Run 3 as an example once again, by substituting the appropriate values into Equation (8) of Section VIII, we

appropriate values into Equation (8) of Section VIII, we

of Run 3 as an example once again, by substituting the

small percentage of the total volume of vapor. Using Point 4

temperature T_v , inasmuch as these two factors are only a

0.02% in the calculation of the vapor density, d_v , at the

Section VIII). This, however, leads to an error of only

calculation of the factors $V_{A,0}$ and $V_{C,0}$ (Equation 3 of

assumption introduces an error of approximately 4.2% into the

solid vapor at each setting of thermostat "A". Such an

it is possible to calculate the density of triphenylacetic

the vapor density at 55.53° the vapor density at 50.76°

at 151.25° the vapor density at 158° and, similarly, that

Operating on the assumption that the vapor density

$$(T_{v1})_3 = 1.5688 \times 10^{-3} \text{ gm./cc.}$$

$$(T_{v2})_3 = 3.1054 \times 10^{-3} \text{ gm./cc.}$$

Equations (6) and solving

Re substituting these new values for the vapor density into

$$(T_{v1})_2 = 1.5688 \times 10^{-3} \text{ gm./cc.}$$

$$(T_{v2})_2 = 3.1054 \times 10^{-3} \text{ gm./cc.}$$

from which we obtain that

$$(T_{v2})_2 = \frac{3.0868 - (1.6193)(1.4135) - (5.2380)(338.79/441.15)}{(1.5773 \times 10^{-3}) - (1.0934)(424.51/323.92)(3.0814 \times 10^{-3})} = 3.1054 \times 10^{-3}$$

$$(T_{v1})_2 = \frac{3.0868 - (1.6193)(1.4135) - (5.2380)(424.51/441.15)}{(1.5773 \times 10^{-3}) - (1.0934)(424.51/323.92)(3.0814 \times 10^{-3})} = 1.5688 \times 10^{-3}$$

Substituting in Equations (6), we obtain,

obtain

$$d_v = \frac{3.0868 - (1.7536)(1.4135) - (5.280)(1.5688 \times 10^{-3}) - (1.2328)(3.1054 \times 10^{-3})}{253.730}$$

$$= 2.3489 \times 10^{-3} \text{ gm./cc.}$$

which is the density of trifluoroacetic acid vapor at 97.08° and at a pressure of 0.45 atm.

Employing the perfect gas law, the apparent molecular weight of the vapor is calculated:

$$M_v = \frac{(2.3489 \times 10^{-3})(82.05)(273.16 + 97.08)}{0.45}$$

$$= \cancel{158.56} 158.56$$

By precisely the same methods, the values of Tables 9-15 have been calculated. The isobaric curves of the molecular weight at various temperatures are plotted in Figure 16. Since it is more convenient to deal with the corresponding isotherms, the family of curves of Figure 16 were cross-read at convenient temperatures. This procedure yielded the data tabulated in Table 16. A graphical representation of the isotherms of the molecular weight at various pressures is given in Figure 17.

obtain

$$\delta_v = \frac{3.0888 - (1.7338)(1.4135) - (5.289)(1.5588 \times 10^{-3}) - (1.3228)(3.1054 \times 10^{-5})}{253.750}$$

253.750

$$= 2.3483 \times 10^{-3} \text{ gm./cc.}$$

which is the density of trifluoroacetic acid vapor at 37.38°

and at a pressure of 0.45 atm.

Employing the perfect gas law, the apparent molecu-

lar weight of the vapor is calculated:

$$M_v = \frac{(2.3483 \times 10^{-3})(32.03)(273.16)(37.38)}{0.45}$$

$$= 158.56 \text{ g./mole}$$

By precisely the same methods, the values of Tables

9-15 have been calculated. The isobaric curves of the

molecular weight at various temperatures are plotted in

Figure 16. Since it is more convenient to deal with the cor-

responding isotherms, the family of curves of Figure 16 were

cross-read at convenient temperatures. This procedure yielded

the data tabulated in Table 16. A graphical representation

of the isotherms of the molecular weight at various pressures

is given in Figure 17.

Table 9

Run 1 - Evaluation of the Vapor Density
(180 mm. = 0.237 atm.)

Point	$T_v (^{\circ}\text{C.})$	$V_1 (\text{cc.})$	$V_v (\text{cc.})$	$V_b (\text{cc.})$	$d (\times 10^3)$ (gm./cc.)	M_v
1	50.53	1.8366	253.432	1.1488	1.6436	181.89
2	60.68	1.8604	253.496	1.1250	1.5029	171.53
3	70.44	1.8782	253.558	1.1072	1.4009	164.56
4	80.39	1.9004	253.621	1.0850	1.2734	153.92
5	91.41	1.9213	253.689	1.0641	1.1537	143.80
6	100.92	1.9371	253.750	1.0483	1.0633	135.99
7	111.21	1.9481	253.816	1.0373	1.0000	131.41
8	121.43	1.9605	253.879	1.0249	0.9290	125.32
9	131.28	1.9695	253.943	1.0159	0.8776	121.35
10	141.42	1.9762	254.006	1.0092	0.8389	118.90
11	153.77	1.9846	254.084	1.0008	0.7891	115.18

$$T_1 (= T_b) = 35.58^{\circ} \text{C.}; T_a = 181^{\circ} \text{C.}; V_a = 5.282 \text{ cc.}$$

$$W = 3.0868 \text{ gm.}; \rho = 1.4512 \text{ gm./cc.}$$

$$M = 2.0000 \text{ cm} : b = 1.4975 \text{ cm} \setminus \text{cm}.$$

$$I^1 (= \Delta^2) = 90.00 \text{ cm} : \Delta^2 = 181.0 \text{ cm} : \Delta^2 = 2.822 \text{ cm}.$$

11	129.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
12	141.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
13	151.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
14	161.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
15	171.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
16	181.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
17	191.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
18	201.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
19	211.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
20	221.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
21	231.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
22	241.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
23	251.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
24	261.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
25	271.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
26	281.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
27	291.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
28	301.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
29	311.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0
30	321.41	1.0000	90.00	90.00	1.0000	181.0	181.0	181.0

$\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$ $\Delta^2 (0.0)$

(190 cm = 0.821 cm)
 (190 cm = 0.821 cm)

Table 10

Run 2 - Evaluation of the Vapor Density
(247 mm. = 0.325 atm.)

Point	$T_v(^{\circ}\text{C.})$	$V_l(\text{cc.})$	$V_v(\text{cc.})$	$V_b(\text{cc.})$	$d(\times 10^3)$ (gm./cc.)	M_v
1	56.27	1.7429	253.469	1.2429	2.2891	193.36
2	67.85	1.7757	253.540	1.2101	2.1030	183.88
3	77.51	1.8072	253.603	1.1786	1.9249	173.08
4	87.94	1.8337	253.679	1.1521	1.7748	164.33
5	98.08	1.8600	253.730	1.1258	1.6261	154.79
6	107.81	1.8859	253.806	1.0999	1.4797	144.54
7	117.75	1.9082	253.857	1.0776	1.3539	135.70
8	127.87	1.9223	253.933	1.0635	1.2741	131.01
9	138.15	1.9334	253.983	1.0524	1.2110	127.72
10	150.77	1.9455	254.059	1.0403	1.1426	124.20

$$T_l (= T_b) = 42.84^{\circ} \text{C.}; T_a = 175^{\circ} \text{C.}; V_a = 5.281 \text{ cc.};$$

$$W = 3.0868 \text{ gm.}; \rho = 1.4331 \text{ gm./cc.}$$

Table 11

Run 3 - Evaluation of the Vapor Density
(343 mm. = 0.451 atm.)

Point	$T_v (^{\circ}\text{C.})$	$V_l (\text{cc.})$	$V_v (\text{cc.})$	$V_b (\text{cc.})$	$d (\times 10^3)$ (gm./cc.)	M_v
1	65.63	1.6192	253.527	1.3672	3.0986	191.41
2	76.83	1.6756	253.598	1.3108	2.7837	177.64
3	86.79	1.7144	253.654	1.2720	2.5675	168.50
4	97.08	1.7536	253.730	1.2328	2.3489	158.56
5	107.42	1.7886	253.781	1.1978	2.1538	149.45
6	117.71	1.8178	253.857	1.1686	1.9908	141.88
7	127.70	1.8542	253.920	1.1322	1.7884	130.71
8	137.69	1.8717	253.983	1.1147	1.6909	126.67
9	151.35	1.8930	254.069	1.0934	1.5717	121.65

$$T_l (= T_b) = 50.76^{\circ}\text{C.}; T_a = 168^{\circ}\text{C.}; V_a = 5.280^{\circ}\text{C.};$$

$$w = 3.0868 \text{ gm.}; \rho = 1.4135 \text{ gm./cc.}$$

$$T^I (= T^O =) T^P \quad T^I (= T^O =) T^P$$
$$T^I (= T^O =) T^P \quad T^I (= T^O =) T^P$$

W	($\frac{K}{m} \cdot \frac{1}{m^2}$)	($\frac{1}{m} \cdot \frac{1}{m^2}$)	($\frac{1}{m} \cdot \frac{1}{m^2}$)	($\frac{1}{m} \cdot \frac{1}{m^2}$)	($\frac{1}{m} \cdot \frac{1}{m^2}$)
11.141	6880.3	8735.1	782.233	8210.1	22.22
12.141	7337.8	8012.1	653.233	6870.1	22.22
13.141	8700.3	8878.1	433.233	447.1	27.22
14.141	9832.3	8523.1	017.233	6337.1	20.79
15.141	1631.3	8761.1	187.233	6607.1	24.701
16.141	8000.1	8861.1	733.233	8716.1	17.711
17.141	4337.1	8321.1	038.233	3439.1	07.131
18.141	8000.1	7411.1	233.233	7170.1	20.721
19.141	7172.1	4230.1	000.433	0230.1	22.131

11.141 mm. = 0.441 mm. (1.141 mm. = 0.441 mm.)

11.141 mm.

Table 12

Run 4 - Evaluation of Vapor Density
(470 mm. = 0.618 atm.)

Point	$T_v(^{\circ}\text{C.})$	$V_1(\text{cc.})$	$V_v(\text{cc.})$	$V_b(\text{cc.})$	$d(\times 10^3)$ (gm./cc.)	M_v
1	70.32	1.4241	253.558	1.5629	4.2733	194.25
2	81.37	1.4926	253.626	1.4944	3.8967	182.83
3	91.12	1.5603	253.689	1.4267	3.5248	169.93
4	101.01	1.6088	253.750	1.3782	3.2584	161.35
5	112.13	1.6685	253.821	1.3185	2.9307	149.43
6	121.60	1.7115	253.881	1.2755	2.6948	140.78
7	131.64	1.7462	253.945	1.2408	2.5041	134.15
8	141.32	1.7754	254.006	1.2116	2.3437	128.56
9	155.60	1.8088	254.097	1.1782	2.1601	122.57

$$T_1 (= T_b) = 58.57^{\circ} \text{C.}; T_a = 172^{\circ} \text{C.}; V_a = 5.281 \text{ cc.};$$

$$w = 3.0868 \text{ gm.}; \rho = 1.3940 \text{ gm./cc.}$$

$$p = 1.2340 \text{ atm} \cdot \text{cc} \cdot \text{g}^{-1}$$

$$T = 20.25^\circ \text{C} : T^0 = 18.0^\circ \text{C} : V^0 = 2.581 \text{ cc} :$$

$$p^0 = 3.0368 \text{ atm} :$$

$$T^0 = 18.0^\circ \text{C} : T^0 = 18.0^\circ \text{C} : V^0 = 2.581 \text{ cc} :$$

Point	$T^0 (^\circ \text{C})$	$T (^\circ \text{C})$	$V (^\circ \text{C})$	$V^0 (^\circ \text{C})$	$p (^\circ \text{C})$	$p^0 (^\circ \text{C})$	$\rho (^\circ \text{C})$	$\rho^0 (^\circ \text{C})$
1	10.25	14.84	222.228	222.228	1.2038	1.2038	1.2038	1.2038
2	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
3	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
4	10.101	14.84	222.228	222.228	1.2038	1.2038	1.2038	1.2038
5	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
6	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
7	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
8	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
9	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
10	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
11	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
12	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
13	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
14	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
15	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
16	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
17	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
18	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
19	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038
20	11.12	15.62	222.228	222.228	1.2038	1.2038	1.2038	1.2038

Run # - Evaluation of Vapor Density
(V^0 mm = 0.278 atm.)

Table 13

Table 13

Run 5 - Evaluation of the Vapor Density

(605 mm. = 0.796 atm.)

Point	$T_v (^{\circ} \text{C.})$	$V_l (\text{cc.})$	$V_v (\text{cc.})$	$V_b (\text{cc.})$	$d (\times 10^3)$ (gm./cc.)	M_v
1	78.08	1.2870	253.606	1.7006	5.0885	183.30
2	87.88	1.3576	253.668	1.6300	4.7055	174.24
3	97.89	1.4318	253.732	1.5558	4.3030	163.75
4	108.94	1.5021	253.801	1.4855	3.9218	153.69
5	118.59	1.5603	253.862	1.4273	3.6061	144.89
6	128.57	1.6115	253.925	1.3761	3.3286	137.14
7	139.38	1.6567	253.993	1.3309	3.0834	130.46
8	151.96	1.6984	254.074	1.2892	2.8573	124.58

$$T_l \neq (= T_b) = 65.34^{\circ} \text{C.}; T_a = 165^{\circ} \text{C.}; V_a = 5.280 \text{ cc.};$$

$$W = 3.0868 \text{ gm.}; \rho = 1.3773 \text{ gm./cc.}$$

$$M = 2.0828 \text{ gm.} \quad b = 1.2112 \text{ gm./cc.}$$

$$V^L (\text{cc.}) = 22.34 \quad V^G (\text{cc.}) = 122.0 \quad V^S (\text{cc.}) = 2.580 \text{ cc.}$$

8	121.20	1.0334	824.014	1.3835	3.2212	124.28
7	120.38	1.0224	823.832	1.3206	3.0824	120.40
6	118.24	1.0112	822.852	1.2481	3.2580	121.14
5	118.20	1.0003	822.808	1.4512	3.0091	144.83
4	108.34	1.2051	822.801	1.4822	3.6518	122.03
3	84.80	1.4218	822.438	1.2228	4.2920	103.12
2	84.88	1.2242	822.008	1.0200	4.1020	114.53
1	48.08	1.5540	822.000	1.1002	2.0882	182.20

Point	$M^A (\text{cc.})$	$V^A (\text{cc.})$	$V^P (\text{cc.})$	$(M^A \backslash \text{cc.})$ $q(x_{10_2})$	M^A
-------	--------------------	--------------------	--------------------	--	-------

$$(100 \text{ mm}^3 = 0.146 \text{ gmm}^3)$$

Run 2 - Evaluation of the Asbol Density

Table 13

Table 14

Run 6 - Evaluation of Vapor Density
(780 mm. = 1.03 atm.)

Point	$T_v (^{\circ}\text{C.})$	$V_1 (\text{cc.})$	$V_v (\text{cc.})$	$V_b (\text{cc.})$	$d (\times 10^3)$ (gm./cc.)	M_v
1	86.33	1.0608	253.659	1.9273	6.3688	182.38
2	93.91	1.1335	253.707	1.8546	5.9656	174.44
3	103.71	1.2308	253.768	1.7573	5.4449	163.46
4	114.50	1.3192	253.836	1.6689	4.9721	153.54
5	125.74	1.4012	253.907	1.5869	4.5333	144.05
6	136.15	1.4671	253.973	1.5210	4.1809	136.32
7	146.08	1.5222	254.036	1.4659	3.8865	129.80
8	154.83	1.5554	254.092	1.4327	3.7042	126.29

$T_1 (= T_b) = 72.17^{\circ}\text{C.}; T_a = 180^{\circ}\text{C.}; V_a = 5.282\text{ cc.};$

$m = 3.0868\text{ gm.}; \rho = 1.3603\text{ gm./cc.}$

$$M = 3.0898 \text{ gm.} \quad b = 1.2902 \text{ gm./cc.}$$

$$T^T (= T^P) = 15.11^\circ \text{C.} : T^W = 180^\circ \text{C.} : V^W = 2.368 \text{ cc.}$$

Point	$T^A (^\circ \text{C.})$	$T^T (^\circ \text{C.})$	$T^V (^\circ \text{C.})$	$T^P (^\circ \text{C.})$	(gm./cc.) $\rho(x\text{H}_2\text{O}_2)$	M^A
8	124.84	1.2224	824.028	1.2324	2.1043	182.88
7	149.08	1.2384	830.438	1.2424	2.3322	182.80
6	120.12	1.4247	822.532	1.2570	4.1808	130.28
5	132.47	1.4072	822.803	1.2628	4.2222	140.41
4	114.20	1.2128	822.823	1.2688	4.2431	122.24
3	102.17	1.3228	822.198	1.2742	2.4443	122.42
2	82.37	1.7222	822.101	1.2842	2.2222	114.44
1	22.22	1.0208	822.222	1.2843	2.2222	182.28

Run 8 - Examination of Ascorbic Acid
(180 mm. = 1.02 mm.)

Table 14

Table 15

Run 7 - Evaluation of Vapor Density
(951 mm. = 1.25 atm.)

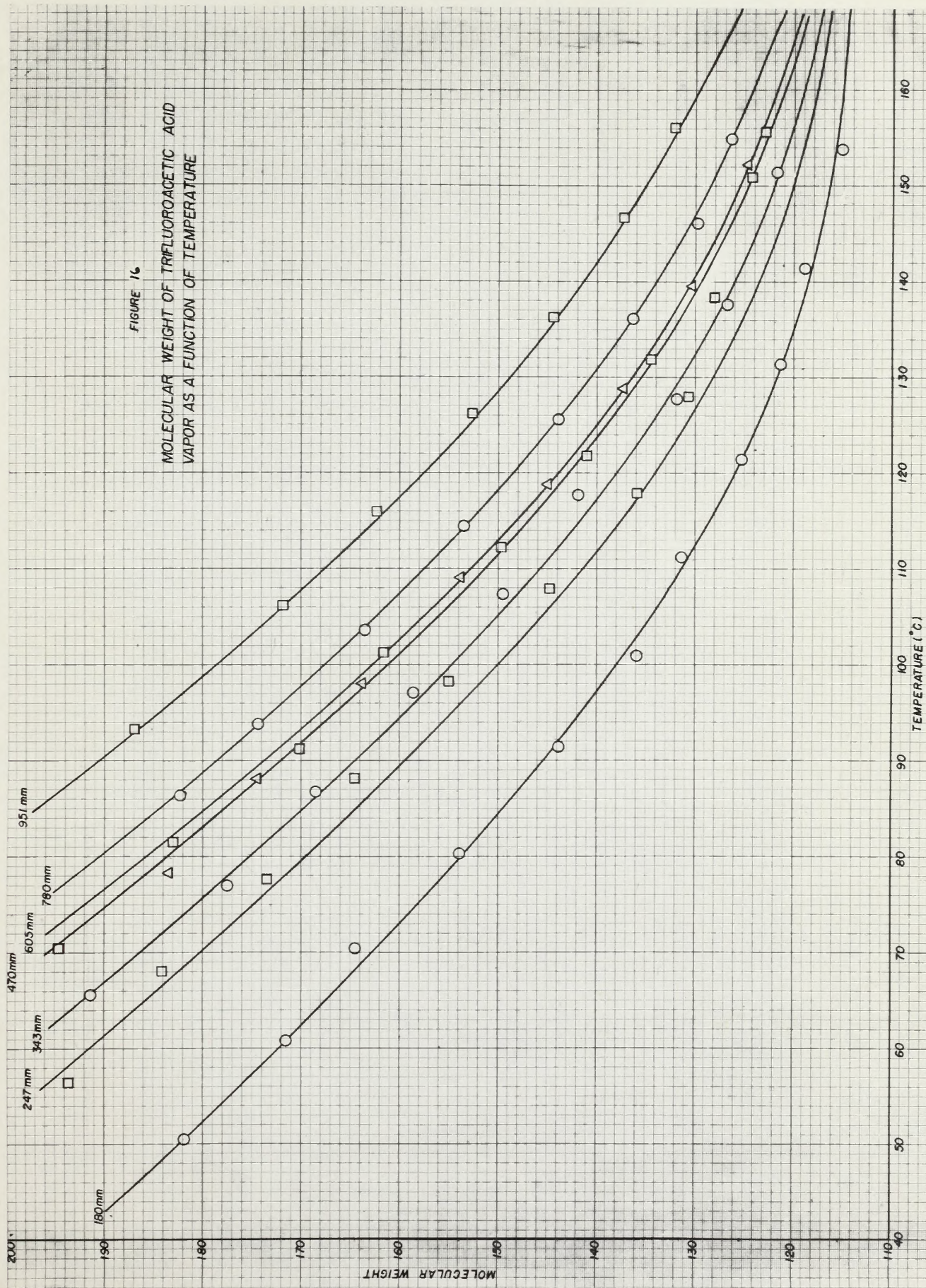
Point	$T_v(^{\circ}\text{C.})$	$V_l(\text{cc.})$	$V_v(\text{cc.})$	$V_b(\text{cc.})$	$d(\times 10^3)$ (gm./cc.)	M_v
1	93.09	0.8019	253.702	2.1866	7.7636	186.64
2	105.97	0.9625	253.783	2.0260	6.8990	171.69
3	115.83	1.0664	253.844	1.9221	6.3494	162.12
4	125.88	1.1671	253.910	1.8214	5.8172	152.37
5	136.20	1.2523	253.973	1.7362	5.3667	144.21
6	146.52	1.3260	254.039	1.6625	4.9771	137.11
7	156.01	1.3811	254.100	1.6074	4.6794	131.82

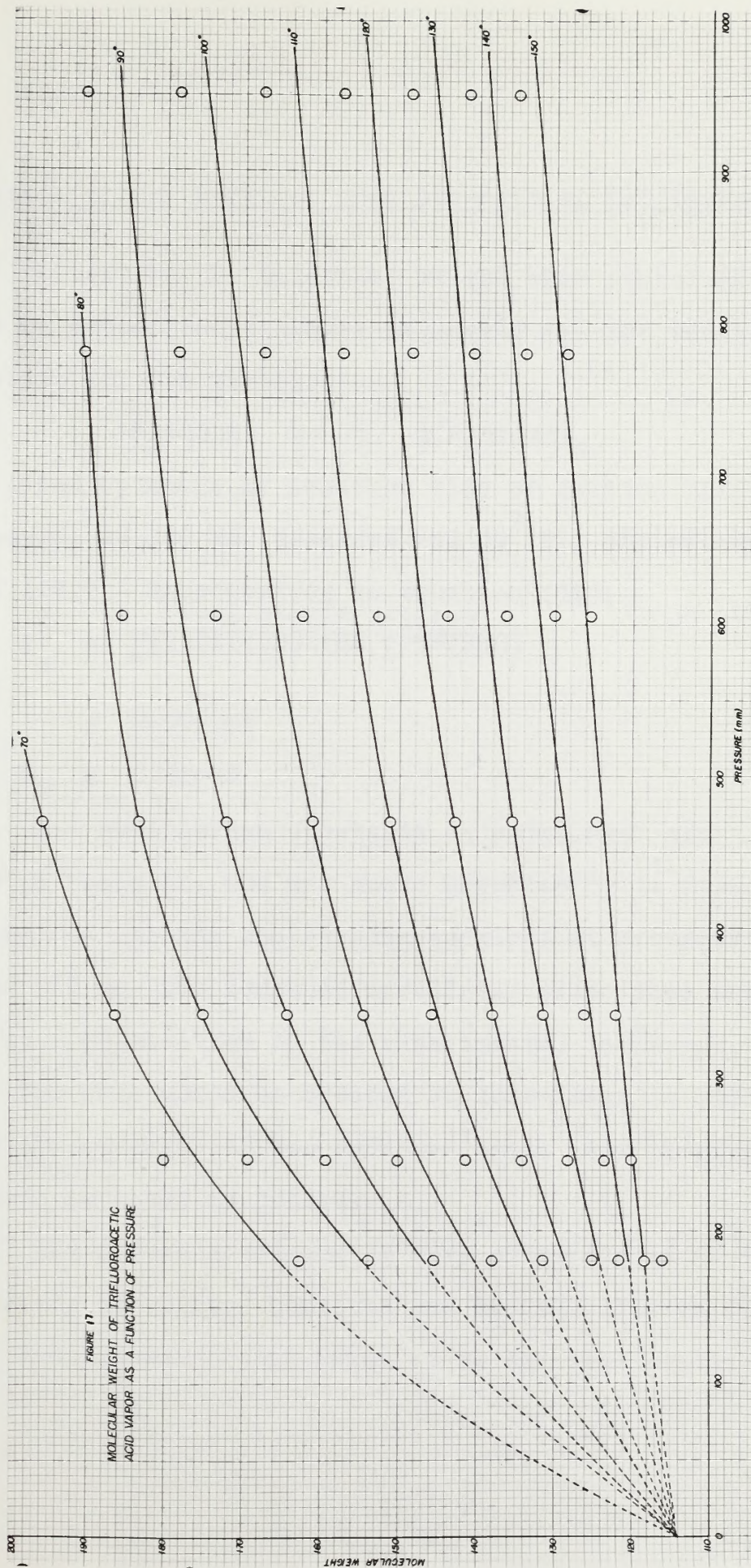
$$T_l (= T_b) = 77.92^{\circ}\text{C.}; T_a = 178^{\circ}\text{C.}; V_a = 5.282\text{ cc.};$$

$$W = 3.0868\text{ gm.}; \quad \rho = 1.3460\text{ gm./cc.}$$

Table 16
Isotherms Obtained from Figure 16

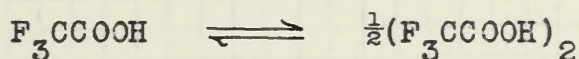
P (mm.)	70°	80°	90°	100°	110°	120°	130°	140°	150°
180	162.7	152.8	145.4	137.9	131.4	125.0	121.6	118.2	116.0
247	180.2	169.4	159.4	150.1	141.4	134.1	128.2	123.5	120.0
342	186.4	175.2	164.4	154.6	145.8	138.0	131.4	126.1	122.0
470	195.8	183.5	172.2	161.2	151.2	142.9	135.5	129.4	124.6
605		185.8	173.8	162.6	152.9	144.0	136.4	130.1	125.5
780		190.6	178.6	167.6	157.6	148.6	140.7	134.0	128.6
951			190.5	178.5	167.7	157.6	148.8	141.3	135.0





Determination of the Hydrogen Bond Strength of Trifluoroacetic Acid.

Values for the molecular weight were picked off the isotherms at convenient pressure intervals and the equilibrium constant for the process



was calculated by means of equation (15) of Section VIII.

As an example, at 350 mm. pressure and 90° C., the molecular weight is 165.0. Substituting in equation (15),

$$K_d = \frac{(114.0)(165.0 - 114.0)}{(2)(114.0 - 165.0)(350)}$$

$$= 0.004185$$

$$K_d = 0.06469$$

The equilibrium constants so calculated are presented in Table 17, and are shown graphically in Figure 18. The values for the equilibrium constant at pressures lower than 180 mm. are somewhat unreliable since they are obtained by extrapolation of the experimental isotherms.

The data could be treated in three ways to yield a value for the strength of the hydrogen bond. All three procedures were employed as follows.

The curves of Figure 18 were extrapolated to zero pressure along the sloped portions and the equilibrium constants at zero pressure were taken to be the true equilibrium

Determination of the Hydrogen Bond Strength of Trifluoroacetic Acid.

Values for the molecular weight were picked off the isotherms at convenient pressure intervals and the equilibrium constant for the process



was calculated by means of equation (15) of Section VIII. As an example, at 350 mm. pressure and 80° C., the molecular weight is 155.0. Substituting in equation (15),

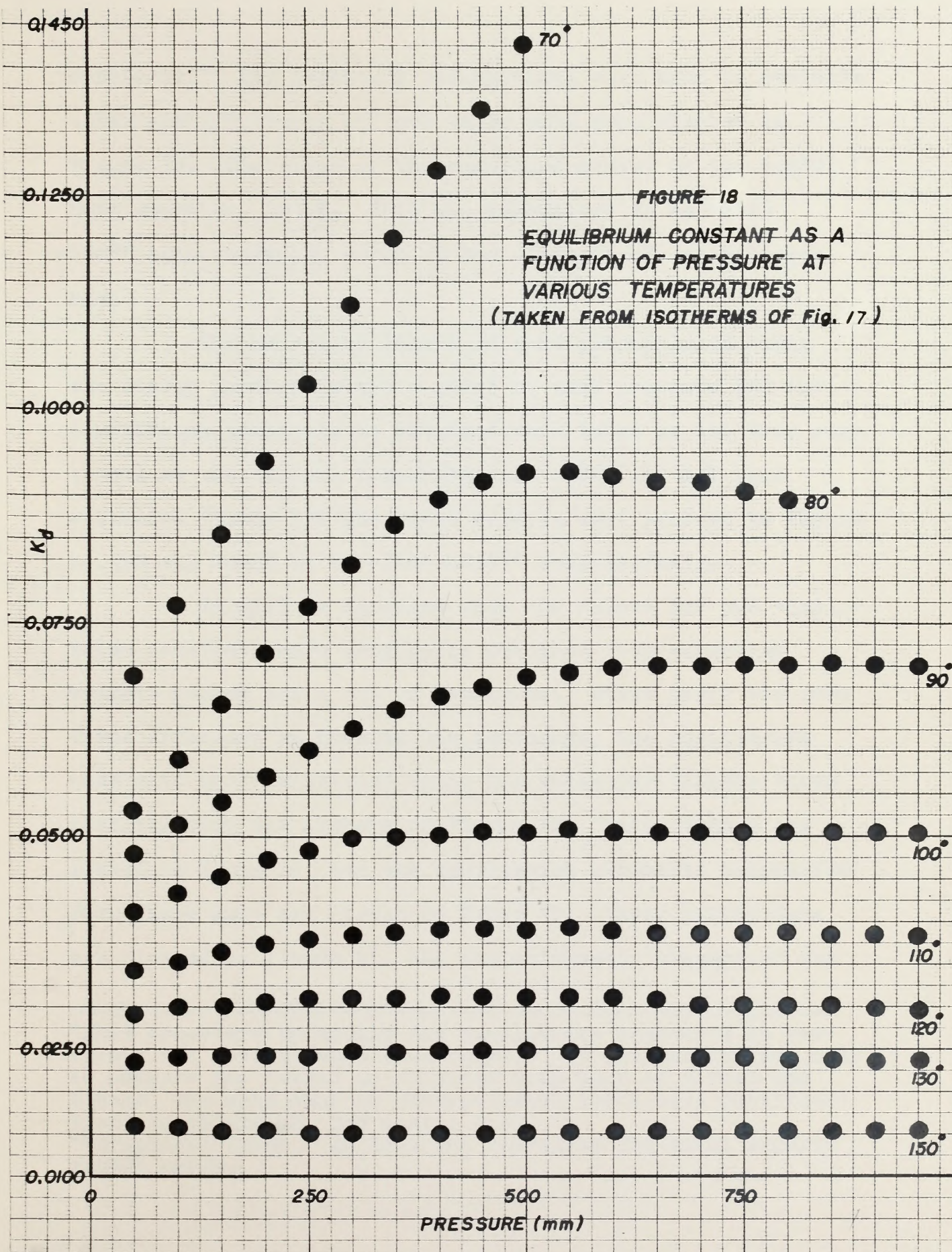
$$\frac{K_p}{K_d} = \frac{(114.0)(155.0 - 114.0)}{(155.0)^2} = 0.004185$$

$$K_p = 0.004185$$

$$K_d = 0.004185$$

The equilibrium constants so calculated are presented in Table IV, and are shown graphically in Figure 18. The values for the equilibrium constant at pressures lower than 180 mm. are somewhat unreliable since they are obtained by extrapolation of the experimental isotherms. The data could be treated in three ways to yield a value for the strength of the hydrogen bond. All three procedures were employed as follows.

The curves of Figure 18 were extrapolated to zero pressure along the sloped portions and the equilibrium constants at zero pressure were taken to be the true equilibrium



constants.* The necessary calculations were made to evaluate $-R\ln K$ and $1/T$ (Table 18) and these data were plotted in Figure 19. The slope of the resultant curve, by the van't Hoff equation, is ΔH . This was calculated to be $-4225 \pm 600^{**}$ calories/mole, which is the strength of one hydrogen bond.

The curves of Figure 18 were extrapolated along the linear portion (slope = zero) to zero pressure and the equilibrium constants so obtained were taken as the true constants at the various temperatures. $-R\ln K$ and $1/T$ were evaluated (Table 19) and these results were plotted in Figure 20. ΔH was found to be $-7000 \pm 250^{**}$ calories/mole.

It will be recalled that the values for the equilibrium constants were originally obtained from molecular weights picked off a set of isotherms. Since there was some error attendant on drawing the isotherms, the equilibrium constants were calculated using the molecular weights taken directly from the isobars of Figure 16. These values are listed in Table 16, and the equilibrium constants calculated from these data are listed in Table 20. These latter data are plotted in Figure 21, and the arithmetic average of the

*This procedure to obtain the equilibrium constants is certainly not good science (see below). It was carried out only to compare the result so obtained with that of Ritter and Simons, who used such an extrapolation (with more justification) to obtain ΔH for acetic acid.

**Graphical error. It does not represent the total experimental error.

constants. The necessary calculations were made to evaluate ΔH and ΔT (Table 18) and these data were plotted in Figure 19. The slope of the resultant curve, by the van't Hoff equation, is ΔH . This was calculated to be -4825 cal/mole. The strength of one hydrogen bond is 4800 cal/mole.

The curves of Figure 18 were extrapolated along the linear portion (slope = zero) to zero pressure and the equilibrium constants so obtained were taken as the true constants at the various temperatures. ΔH and ΔT were evaluated (Table 19) and these results were plotted in Figure 20. ΔH was found to be -7000 cal/mole.

It will be recalled that the values for the equilibrium constants were originally obtained from molecular weights picked off a set of isotherms. Since there was some error attendant on drawing the isotherms, the equilibrium constants were calculated using the molecular weights taken directly from the isotherms of Figure 15. These values are listed in Table 15, and the equilibrium constants calculated from these data are listed in Table 20. These latter data are plotted in Figure 21, and the arithmetic average of the

*This procedure to use in the equilibrium constants is certainly not good science (see below). It was carried out only to compare the results obtained with that of Ristic and Simon, who used such an extrapolation (also more justified than) to obtain ΔH for acetic acid.
 **Graphical error. It does not represent the total experimental error.

Table 17

Equilibrium Constants Calculated from the Isotherms of Figure 17

Pres- sure (mm.)	70° Isotherm				80° Isotherm				90° Isotherm				100° Isotherm			
	Molec- ular Weight	K_d^2 ($\times 10^3$)	K_d ($\times 10^2$)	Molec- ular Weight	K_d^2 ($\times 10^3$)	K_d ($\times 10^2$)	Molec- ular Weight	K_d^2 ($\times 10^3$)	K_d ($\times 10^2$)	Molec- ular Weight	K_d^2 ($\times 10^3$)	K_d ($\times 10^2$)	Molec- ular Weight	K_d^2 ($\times 10^3$)	K_d ($\times 10^2$)	Molec- ular Weight
50	132.8	4.73	6.88	126.6	2.79	5.29	124.8	2.31	4.81	122.3	1.69	4.12				
100	147.6	5.93	7.70	138.5	3.49	5.91	134.2	2.62	5.12	129.8	1.87	4.32				
150	159.4	7.33	8.56	149.2	4.31	6.56	142.3	2.93	5.41	136.6	2.06	4.53				
200	168.6	8.82	9.39	157.9	5.09	7.14	149.5	3.28	5.73	142.4	2.21	4.70				
250	176.2	10.6	10.3	165.2	5.92	7.69	155.6	3.62	6.02	147.5	2.36	4.86				
300	182.4	12.5	11.2	171.1	6.70	8.19	160.6	3.90	6.24	151.7	2.46	4.96				
350	187.4	14.3	12.0	176.0	7.47	8.64	165.0	4.19	6.47	155.0	2.51	5.01				
400	191.3	16.4	12.8	179.7	8.03	8.96	168.6	4.41	6.64	157.8	2.53	5.03				
450	194.6	18.3	13.5	182.6	8.43	9.18	171.6	4.59	6.77	160.4	2.57	5.07				
500	197.4	20.3	14.3	184.8	8.65	9.30	174.1	4.72	6.87	162.4	2.56	5.06				
550				186.4	8.67	9.31	176.2	4.81	6.93	164.4	2.58	5.08				
600				187.6	8.57	9.26	178.0	4.86	6.97	166.0	2.57	5.07				
650				188.6	8.43	9.18	179.5	4.88	6.99	167.4	2.55	5.05				
700				189.6	8.35	9.14	180.8	4.88	6.99	168.8	2.55	5.05				
750				190.4	8.21	9.06	182.1	4.91	7.01	170.1	2.54	5.04				
800				191.0	8.02	8.95	183.2	4.91	7.01	171.3	2.54	5.04				
850							184.3	4.94	7.03	172.6	2.56	5.06				
900							185.2	4.92	7.02	173.8	2.58	5.08				
950							186.1	4.93	7.02	175.0	2.61	5.11				

Table 17
(concluded)

Equilibrium Constants Calculated from the Isotherms of Figure 17

Pres- sure (mm.)	110° Isotherm			120° Isotherm			130° Isotherm			150° Isotherm		
	Molec- ular Weight	K_d ($\times 10^3$)	K_d^2 ($\times 10^6$)	Molec- ular Weight	K_d ($\times 10^2$)	K_d^2 ($\times 10^4$)	Molec- ular Weight	K_d ($\times 10^2$)	K_d^2 ($\times 10^4$)	Molec- ular Weight	K_d ($\times 10^2$)	K_d^2 ($\times 10^4$)
50	120.0	1.17	3.43	118.5	8.56	2.93	117.0	5.55	2.36	115.4	2.52	1.59
100	125.4	1.24	3.52	122.7	8.95	2.99	119.9	5.76	2.40	116.7	2.49	1.58
150	130.4	1.31	3.62	126.4	9.13	3.02	122.6	5.88	2.43	117.7	2.31	1.52
200	134.9	1.37	3.71	129.8	9.34	3.06	125.0	5.91	2.43	118.8	2.26	1.50
250	138.9	1.43	3.78	133.0	9.60	3.10	127.2	5.92	2.43	119.8	2.26	1.50
300	142.4	1.47	3.84	135.7	9.68	3.11	129.5	6.07	2.46	120.7	2.21	1.49
350	145.4	1.50	3.87	138.2	9.78	3.13	131.5	6.12	2.47	121.6	2.19	1.48
400	148.1	1.52	3.90	140.4	9.81	3.13	133.3	6.13	2.48	122.5	2.18	1.48
450	150.4	1.53	3.91	142.4	9.82	3.13	134.9	6.11	2.47	123.4	2.18	1.48
500	152.4	1.53	3.91	144.2	9.81	3.13	136.4	6.09	2.47	124.2	2.16	1.47
550	154.2	1.53	3.91	145.8	9.76	3.12	137.6	5.99	2.45	125.2	2.20	1.48
600	155.7	1.52	3.89	147.2	9.66	3.11	138.8	5.92	2.43	126.1	2.21	1.49
650	157.0	1.50	3.86	148.4	9.52	3.09	139.8	5.82	2.41	127.0	2.24	1.50
700	158.2	1.48	3.84	149.4	9.33	3.06	140.7	5.71	2.39	128.0	2.28	1.51
750	159.4	1.47	3.83	150.4	9.19	3.03	141.6	5.62	2.37	129.0	2.33	1.53
800	160.5	1.45	3.81	151.4	9.08	3.01	142.6	5.59	2.36	130.0	2.37	1.54
850	161.6	1.45	3.81	152.4	9.01	3.00	143.6	5.57	2.36	130.8	2.39	1.54
900	162.7	1.45	3.80	153.3	8.92	2.99	144.6	5.57	2.36	131.7	2.42	1.56
950	163.6	1.44	3.79	154.2	8.86	2.98	145.5	5.55	2.36	132.6	2.45	1.57

Table 18

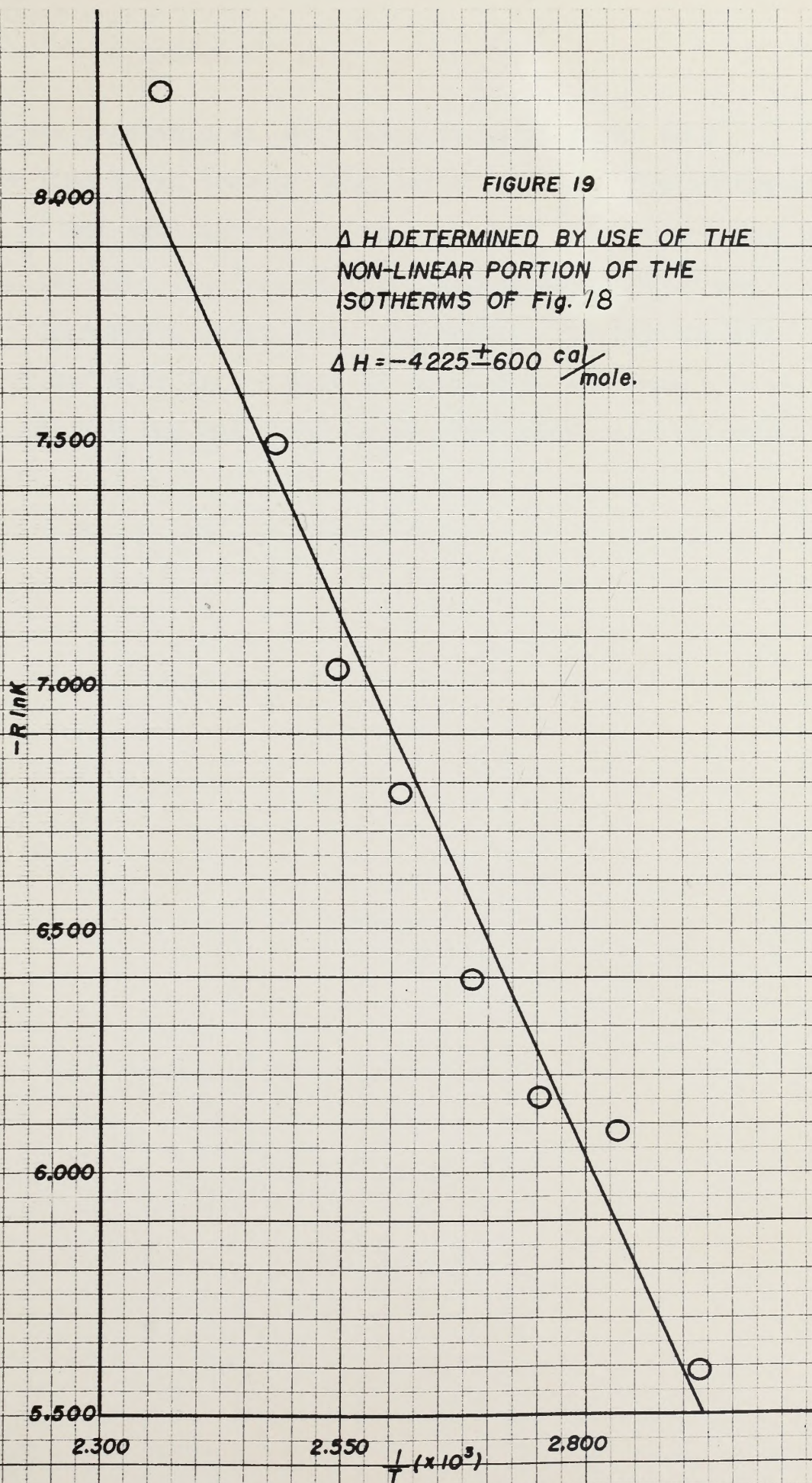
Summary of Calculations to Determine $-R\ln K_d$ and $1/T$
 (K_d obtained from sloped portion of isotherms of Figure 18)

$t(^{\circ}\text{C.})$	$T(^{\circ}\text{K.})$	$1/T \times 10^3$	K_d	$\ln K_d$	$-R\ln K_d$	ΔH
70	343.16	2.914	0.0600	-2.813	5.589	-4225 \pm 600 calories/mole
80	353.16	2.832	0.0468	-3.058	6.076	
90	363.16	2.753	0.0450	-3.102	6.164	
100	373.16	2.680	0.0397	-3.219	6.396	
120	393.16	2.544	0.0286	-3.541	7.036	
130	403.16	2.480	0.0231	-3.773	7.497	
150	423.16	2.363	0.0160	-4.136	8.218	

FIGURE 19

ΔH DETERMINED BY USE OF THE
NON-LINEAR PORTION OF THE
ISOTHERMS OF Fig. 18

$$\Delta H = -4225 \pm 600 \text{ cal/mole.}$$



equilibrium constants at each temperature is shown by a straight line drawn through each set of points. The arithmetic average of the equilibrium constant at each temperature was taken as the true constant at that temperature. $-R\ln K$ and $1/T$ were determined using these constants. The results are presented in Table 21. A plot of these data was made (Figure 22) and ΔH was found to be -7200 ± 250 calories/mole.

acetic acid constant at each temperature is shown by a
straight line drawn through each set of points. The relationship
between the acid constant and each temperature was
found to be linear at these temperatures. The results are
presented in Table II. A plot of these data was made
(Figure 2) and the following equation was found to be applicable:

$$\log K_a = 4.75 - \frac{1000}{T} + 0.0015T$$

Table 19

Summary of Calculations to Determine $-R\ln K_d$ and $1/T$
 (K_d obtained from slope = 0 portion of isotherms of Figure 18)

$t(^{\circ}\text{C.})$	$T(^{\circ}\text{K.})$	$1/T \times 10^3$	K_d	$\ln K_d$	$-R\ln K_d$	ΔH
80	353.16	2.832	0.0914	-2.397	4.763	-7000 \pm 250 calories/mole
90	363.16	2.754	0.0700	-2.660	5.285	
100	373.16	2.680	0.0505	-2.976	5.913	
110	383.16	2.610	0.0382	-3.271	6.499	
120	393.16	2.544	0.0305	-3.474	6.903	
130	403.16	2.480	0.0242	-3.730	7.412	
150	423.16	2.363	0.0156	-4.136	8.218	

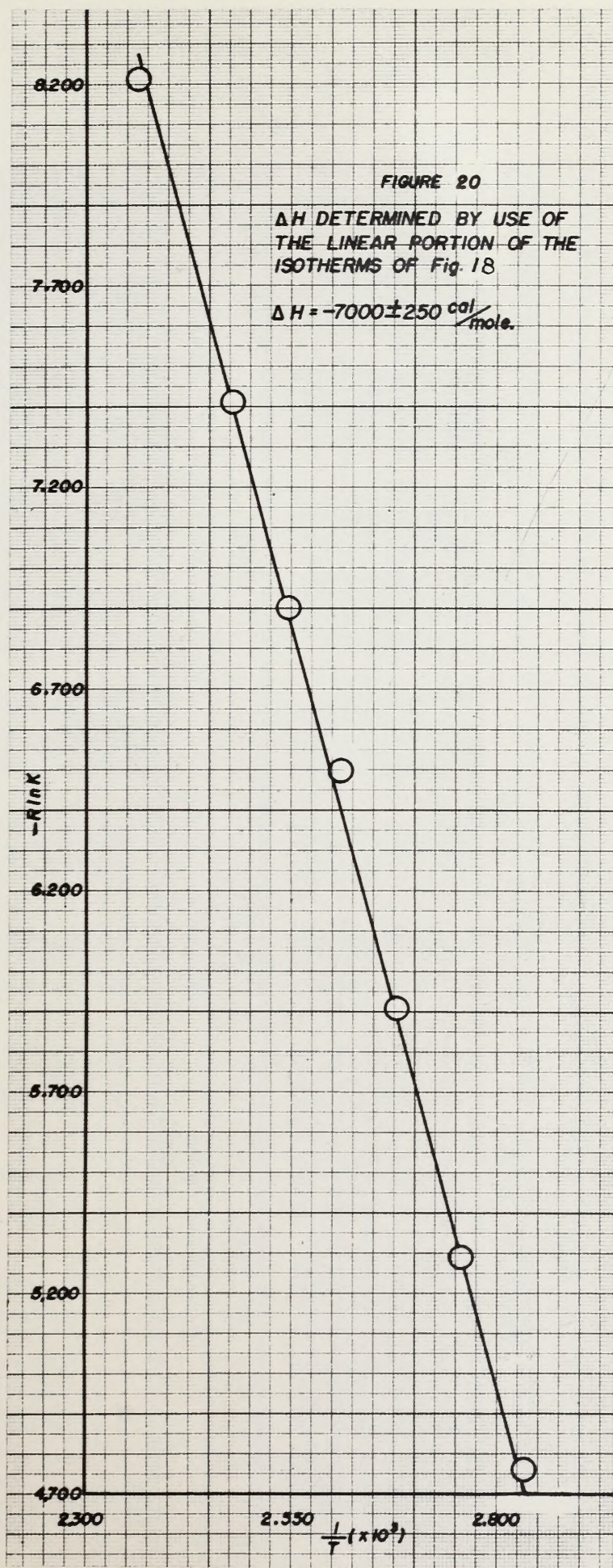


Table 20

Equilibrium Constants Calculated from the Isobars of Figure 16

Pres- sure (mm.)	At 70°			At 80°			At 90°			At 100°		
	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d (10^2)	Molec- ular	Weight	K_d ($\times 10^3$)
180	162.7	7.22	8.50	153.8	4.57	6.76	145.4	2.91	5.40	137.9	1.86	4.31
247	180.2	13.4	11.6	169.4	7.46	8.64	159.4	4.46	6.68	150.1	2.75	5.24
342	186.4	13.9	11.8	175.2	7.31	8.55	164.4	4.15	6.44	154.6	2.51	5.01
470	195.8	19.1	13.8	183.5	8.52	9.23	172.2	4.54	6.73	161.2	2.57	5.07
605				185.8	7.59	8.71	173.8	3.83	6.19	162.6	2.14	4.63
780				190.6	8.01	8.95	178.6	3.87	6.22	167.6	2.15	4.64
951							190.5	6.52	8.08	178.5	3.16	5.62
Average: 11.4			Average: 8.47			Average: 6.53			Average: 4.93			
	At 110°			At 120°			At 130°			At 140°		
	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d (10^2)	Molec- ular	Weight	K_d ($\times 10^3$)
180	131.4	1.18	3.43	125.0	0.656	2.56	121.6	0.425	2.06	118.2	0.220	1.48
247	141.4	1.69	4.11	134.1	1.05	3.25	128.2	0.659	2.57	123.5	0.402	2.01
342	145.8	1.57	3.96	138.0	0.987	3.14	131.4	0.621	2.49	126.1	0.388	1.97
470	151.2	1.53	3.91	142.9	0.968	3.11	135.5	0.610	2.47	129.4	0.384	1.96
605	152.9	1.30	3.60	144.0	0.801	2.83	136.4	0.503	2.24	130.1	0.316	1.78
780	157.6	1.29	3.59	148.6	0.802	2.83	140.7	0.512	2.26	134.0	0.331	1.82
951	167.7	1.77	4.21	157.6	1.06	3.25	148.8	0.665	2.58	141.3	0.436	2.09
Average: 3.83			Average: 3.00			Average: 2.38			Average: 1.87			
	At 150°											
	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d ($\times 10^3$)	Molec- ular	Weight	K_d (10^2)	Molec- ular	Weight	K_d ($\times 10^3$)
180	116.0	0.101	1.00									
247	120.0	0.238	1.54									
342	122.0	0.237	1.54									
470	124.6	0.240	1.55									
605	125.5	0.206	1.44									
780	128.6	0.216	1.47									
951	135.0	0.291	1.70									
Average: 1.46												

vacuum: 7.50

281	122.0	0.280	1.40	0.1	101.0	0.311	0.01
282	123.0	0.210	1.41	0.1	915.0	0.261	0.01
283	124.0	0.200	1.42	0.1	908.0	0.251	0.01
284	125.0	0.280	1.43	0.1	903.0	0.241	0.01
285	126.0	0.280	1.44	0.1	903.0	0.231	0.01
286	127.0	0.280	1.45	0.1	903.0	0.221	0.01
287	128.0	0.280	1.46	0.1	903.0	0.211	0.01
288	129.0	0.280	1.47	0.1	903.0	0.201	0.01
289	130.0	0.280	1.48	0.1	903.0	0.191	0.01
290	131.0	0.280	1.49	0.1	903.0	0.181	0.01

vacuum: 7.50

291	132.0	0.280	1.50	0.1	903.0	0.171	0.01
292	133.0	0.280	1.51	0.1	903.0	0.161	0.01
293	134.0	0.280	1.52	0.1	903.0	0.151	0.01
294	135.0	0.280	1.53	0.1	903.0	0.141	0.01
295	136.0	0.280	1.54	0.1	903.0	0.131	0.01
296	137.0	0.280	1.55	0.1	903.0	0.121	0.01
297	138.0	0.280	1.56	0.1	903.0	0.111	0.01
298	139.0	0.280	1.57	0.1	903.0	0.101	0.01
299	140.0	0.280	1.58	0.1	903.0	0.091	0.01
300	141.0	0.280	1.59	0.1	903.0	0.081	0.01

vacuum: 7.50

301	142.0	0.280	1.60	0.1	903.0	0.071	0.01
302	143.0	0.280	1.61	0.1	903.0	0.061	0.01
303	144.0	0.280	1.62	0.1	903.0	0.051	0.01
304	145.0	0.280	1.63	0.1	903.0	0.041	0.01
305	146.0	0.280	1.64	0.1	903.0	0.031	0.01
306	147.0	0.280	1.65	0.1	903.0	0.021	0.01
307	148.0	0.280	1.66	0.1	903.0	0.011	0.01
308	149.0	0.280	1.67	0.1	903.0	0.001	0.01
309	150.0	0.280	1.68	0.1	903.0	0.001	0.01
310	151.0	0.280	1.69	0.1	903.0	0.001	0.01

vacuum: 7.50

311	152.0	0.280	1.70	0.1	903.0	0.001	0.01
312	153.0	0.280	1.71	0.1	903.0	0.001	0.01
313	154.0	0.280	1.72	0.1	903.0	0.001	0.01
314	155.0	0.280	1.73	0.1	903.0	0.001	0.01
315	156.0	0.280	1.74	0.1	903.0	0.001	0.01
316	157.0	0.280	1.75	0.1	903.0	0.001	0.01
317	158.0	0.280	1.76	0.1	903.0	0.001	0.01
318	159.0	0.280	1.77	0.1	903.0	0.001	0.01
319	160.0	0.280	1.78	0.1	903.0	0.001	0.01
320	161.0	0.280	1.79	0.1	903.0	0.001	0.01

vacuum: 7.50

321	162.0	0.280	1.80	0.1	903.0	0.001	0.01
322	163.0	0.280	1.81	0.1	903.0	0.001	0.01
323	164.0	0.280	1.82	0.1	903.0	0.001	0.01
324	165.0	0.280	1.83	0.1	903.0	0.001	0.01
325	166.0	0.280	1.84	0.1	903.0	0.001	0.01
326	167.0	0.280	1.85	0.1	903.0	0.001	0.01
327	168.0	0.280	1.86	0.1	903.0	0.001	0.01
328	169.0	0.280	1.87	0.1	903.0	0.001	0.01
329	170.0	0.280	1.88	0.1	903.0	0.001	0.01
330	171.0	0.280	1.89	0.1	903.0	0.001	0.01

vacuum: 7.50

331	172.0	0.280	1.90	0.1	903.0	0.001	0.01
332	173.0	0.280	1.91	0.1	903.0	0.001	0.01
333	174.0	0.280	1.92	0.1	903.0	0.001	0.01
334	175.0	0.280	1.93	0.1	903.0	0.001	0.01
335	176.0	0.280	1.94	0.1	903.0	0.001	0.01
336	177.0	0.280	1.95	0.1	903.0	0.001	0.01
337	178.0	0.280	1.96	0.1	903.0	0.001	0.01
338	179.0	0.280	1.97	0.1	903.0	0.001	0.01
339	180.0	0.280	1.98	0.1	903.0	0.001	0.01
340	181.0	0.280	1.99	0.1	903.0	0.001	0.01

FIGURE 21

EQUILIBRIUM CONSTANT AS A
FUNCTION OF PRESSURE AT
VARIOUS TEMPERATURES
(TAKEN DIRECTLY FROM ISOBARS
OF FIGURE 16)

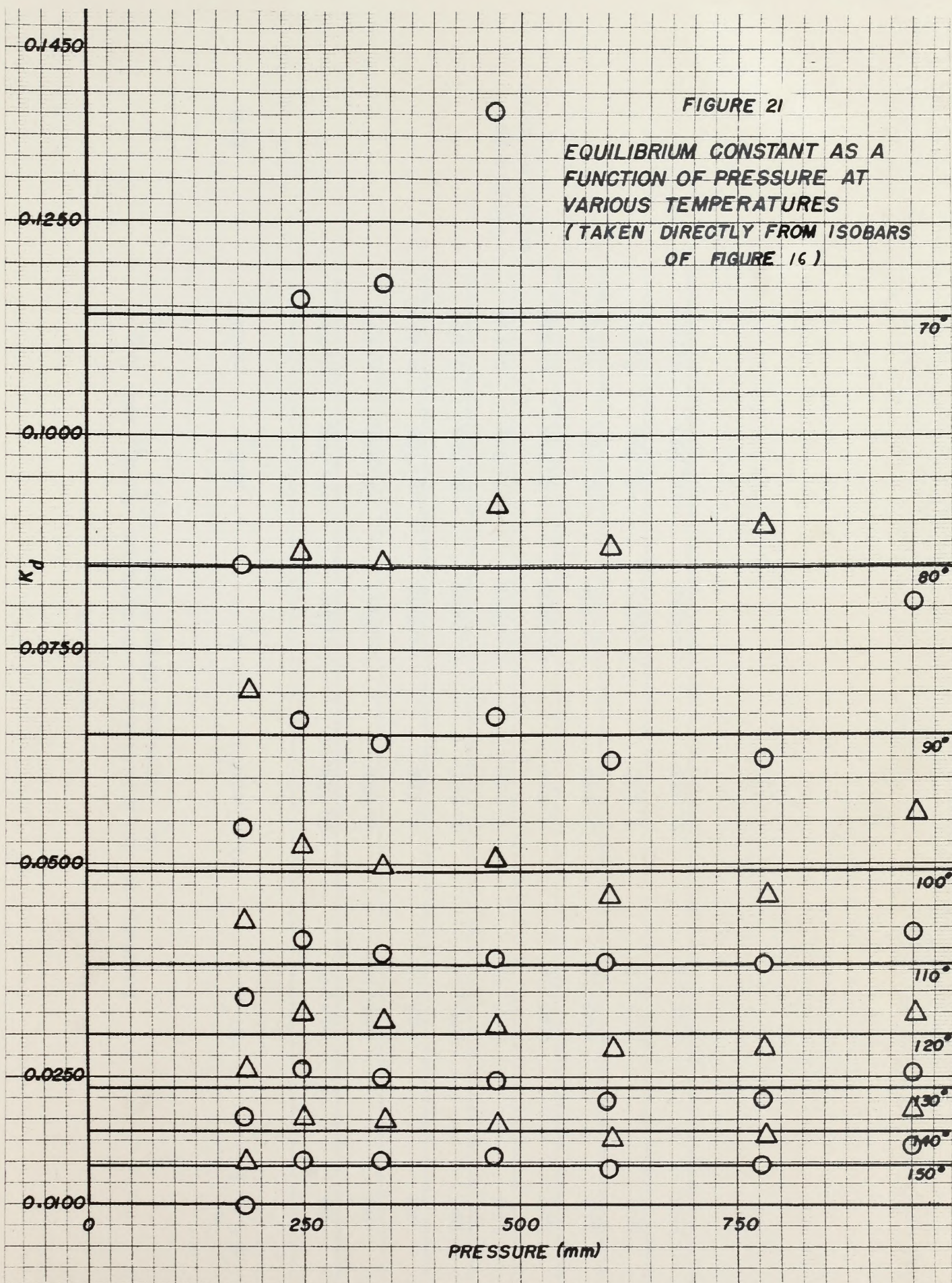
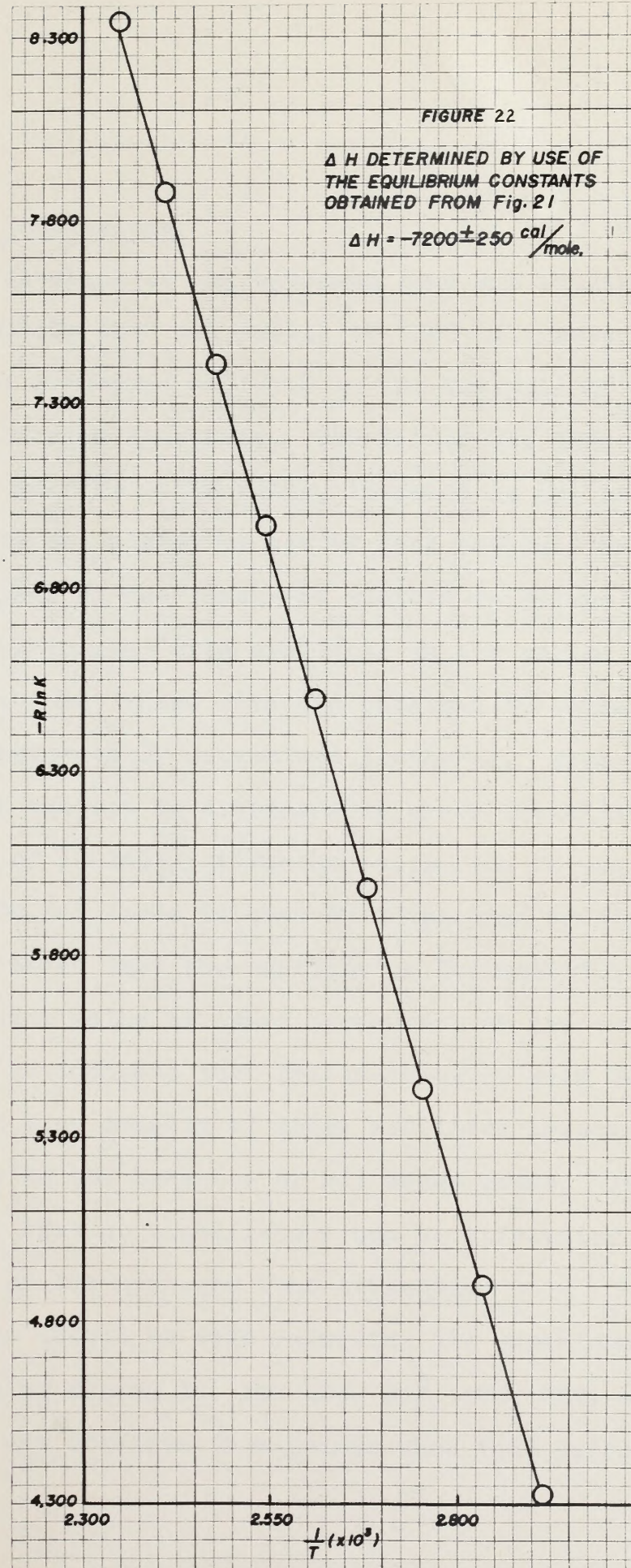


Table 21

Summary of Calculations to Determine $-R\ln K_d$ and $1/T$
 (K_d obtained from Figure 21)

$t(^{\circ}\text{C.})$	$T(^{\circ}\text{K.})$	$1/T(\times 10^3)$	K_d	$\ln K_d$	$-R\ln K_d$	ΔH
70	343.16	2.914	0.114	-2.172	4.316	-7200 \pm 250 calories/mole
80	353.16	2.832	0.0847	-2.466	4.900	
90	363.16	2.753	0.0653	-2.734	5.432	
100	373.16	2.680	0.0493	-3.016	5.993	
110	383.16	2.610	0.0383	-3.271	6.499	
120	393.16	2.544	0.0300	-3.507	6.968	
130	403.16	2.480	0.0238	-3.730	7.412	
140	413.16	2.420	0.0187	-3.964	7.876	
150	423.16	2.363	0.0146	-4.200	8.345	



Discussion and Conclusions.

The strength of the hydrogen bond was evaluated as either approximately 4200 cal./mole, or 7200 cal./mole, depending on the procedure employed in the analysis of the calculated equilibrium constants. The latter has been selected as much the more reliable value, inasmuch as the value of 4200 cal./mole is calculated by use of data obtained from the unreliable portions of the isotherms plotted in Figure 17. There are no experimental data available in the region from 0 to 180 mm. pressure; these data are obtained by extrapolation of the experimentally determined isotherms. Such an extrapolation is subject to considerable error (calculated to be of the order of 10-15%). A further objection to use of the value of 4200 cal./mole is seen by inspection of Figure 18. It will be noted that the equilibrium ~~constant~~ "constant" does not approach a constant value at lower pressures; on the contrary, the curves seem to indicate that trifluoroacetic acid vapor behaves less and less ideally at lower and lower pressures. This is contrary to the behavior of all known gases. It is felt, therefore, that no significance can be attributed to the lower value of the hydrogen bond strength.

A word should be said regarding the experimental data. Referring to Figure 16, the 180, 343, 470, 780, and 951 mm. isobars are obtained from points that fall fairly well

Discussion and Conclusions.

The strength of the hydrogen bond was evaluated as either approximately 4200 cal./mole, or 7800 cal./mole, depending on the procedure employed in the analysis of the calculated equilibrium constants. The latter has been selected as much the more reliable value, inasmuch as the value of 4200 cal./mole is calculated by use of data obtained from the unreliable portions of the isotherms plotted in Figure 17. There are no experimental data available in the region from 0 to 180 mm. pressure; these data are obtained by extrapolation of the experimentally determined isotherms. Such an extrapolation is subject to considerable error (calculated to be of the order of 10-15%). A further objection to use of the value of 4200 cal./mole is seen by inspection of Figure 18. It will be noted that the equilibrium "constant" does not approach a constant value at lower pressures; on the contrary, the curves seem to indicate that trifluoroacetic acid vapor behaves less and less ideally at lower and lower pressures. This is contrary to the behavior of all known gases. It is felt, therefore, that no significance can be attributed to the lower value of the hydrogen bond strength.

A word should be said regarding the experimental data. Referring to Figure 18, the 180, 343, 470, 780, and 951 mm. isotherms are obtained from points that fall fairly well

on the curves as drawn. The 247 and 605 mm. isobars show rather bad scattering around the "best" curves as drawn, particularly the former. The method for drawing the 247 and 605 mm. isobars was simple (and also somewhat unscientific). They were drawn as the best curves possible which would show a change in slope similar to those obtained from the more reliable curves. No explanation is offered for the scattering observed.

If the strength of the hydrogen bond is accepted as being 7200 cal./mole, one is faced with an extremely complex problem in interpretation. Three conclusions may be made on the basis of the observed result: first, the equilibrium constant of trifluoroacetic acid is a true constant for the equilibrium assumed, that is, it behaves as an ideal gas in the pressure range covered; second, implicit in the first conclusion, the order of polymerization of trifluoroacetic acid is no higher than two; third, there is no appreciable difference in the heats of association of trifluoroacetic acid and acetic acid. These conclusions are unexpected.

A number of assumptions were made during the course of the calculations (e.g., the calculation for the meniscus correction, and the approximation method for obtaining the vapor density). These have already been discussed in the appropriate places. It is felt that the error introduced by use of these assumptions is not sufficiently great to affect the results materially.

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It is important to note a serious omission in the evaluation procedure: no correction for adsorption on the walls of the bulb and connecting arm was made. The value of the hydrogen bond strength would be different if this correction were made; it would not account, however, for the unexpectedly high value obtained. It would, indeed, lead to a higher calculated value for the strength of the hydrogen bond, for an adsorption correction would produce a lower value for the vapor density. This would cause a lowering in the apparent molecular weight of the vapor, and, thus, a lowering in the calculated equilibrium constant. Furthermore, the lowering would be greater at lower temperatures (i.e., at larger values of $1/T$) since the error due to adsorption is more serious at lower temperatures. As a result, the slope of the $-R\ln K$ against $1/T$ plot would be increased. Therefore, ΔH would be raised.

A possible method for accounting for the discrepancy between the observed and predicted values would be to assume a systematic error, which is entirely a function of the apparatus. While such a possibility is doubtful in view of the orthodox methods used in this work, it could be confirmed or denied only by determining the hydrogen bond strength of acetic acid in the same apparatus.

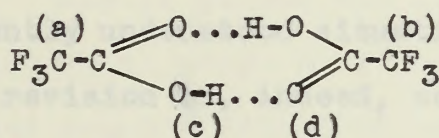
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It will be recalled that in Section I prediction made on the basis of relative electronegativities of substituent groups would tend to indicate that the strength of

the hydrogen bond in trifluoroacetic acid would be less than that in acetic acid. By an extension of the above argument, however, it is possible to rationalize the observed result. Let us consider the dimer as already having been formed, and, furthermore, let us consider the dimer simply as a ring with two strongly polar groups attached to it. We then have the situation



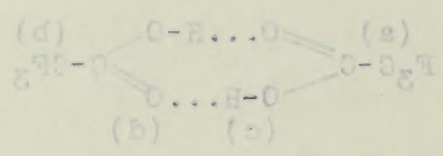
As a first approximation, the net effect will be that groups (a) and (b) negate each other's effect on the ring.

Let us now extend the argument of Section I, in which, it will be recalled, the tacit assumption was made that it was necessary to consider only the two molecules of monomer; this is certainly a serious oversimplification. Let us call the effect of $-\text{CF}_3$ group (a) on the $-\text{O}-\text{H}$ group (c) effect A, and that of $-\text{CF}_3$ group (b) on the $\text{C}=\text{O}$ group (d) effect B. The hydrogen atom of (c) will tend to exert a polarizing effect on the carbonyl oxygen of (d) counter to that of the $-\text{CF}_3$ group (b). Call this effect C. If $|A| + |B| + |C| = 0$, then the net effect of the substituent groups on the hydrogen bond strength will be zero. It will be noted that only one half of the "ring" was discussed; the same argument, of course, applies to the other half of the ring.

If this rationalization is accepted, then one is led to the conclusion that regardless of the substituent group,

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argument, of course, applies to the other half of the ring. If this rationalization is accepted, then one is led to the conclusion that regardless of the substituent group,

the hydrogen bond strengths of all aliphatic carboxylic acids will be essentially the same.

The unsettled nature of the situation at present can not be overemphasized. This is a report on research in progress; a great many things are not yet clarified sufficiently to warrant the presentation of the above argument as a full-blown hypothesis. It may, indeed, be only a rationalization of an insufficiently understood situation, and, therefore, subject to much revision or, indeed, complete rejection, as the laws governing the hydrogen bonding of the carboxylic acids are clarified. It is felt, therefore, that further discussion of the treatment presented above is unwarranted at this time.



It has been variously reported that, on the basis of experimental evidence, acetic acid and propionic acid form polymers of order higher than the dimer, and for acetic acid, the deduction has been made that the next higher polymer is the tetramer.

No investigations have been conducted on the effect of substituents on the strength of the hydrogen bond. It was felt that trifluoroacetic acid would prove interesting in view of the extremely electronegative $-CF_3$ group in the molecule.

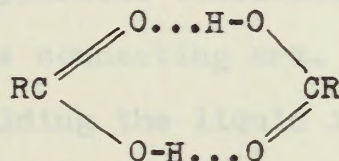
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Abstract.

It has long been recognized that, under certain conditions, an atom of hydrogen is attracted by rather strong forces to two atoms, instead of one, with the result that the hydrogen atom may be visualized as acting as a bond between these two atoms. This is called the hydrogen bond.

The carboxylic acids have been rather extensively studied and values ranging from 6000 to 9000 cal./mole have been reported for the strength of the hydrogen bond. The carboxylic acids are visualized as forming bonds by assuming the structure

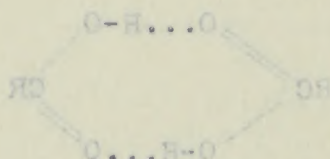


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No investigations have been conducted on the effect of substituents on the strength of the hydrogen bond. It was felt that trifluoroacetic acid would prove interesting in view of the extremely electronegative -CF₃ group in the molecule.

The strength of the hydrogen bond in trifluoroacetic acid was determined in the following way. The vapor density was experimentally determined, and, by making the assumption the the perfect gas law applies to trifluoroacetic acid vapor, the apparent molecular weight of the vapor was calculated as a function of temperature at given pressures. From these isobars, the variation of molecular weight with pressure at given temperatures was determined. The equilibrium constant for the system

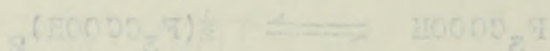


was calculated and by means of the van't Hoff equation, the hydrogen bond strength was evaluated.

The apparatus consisted of a bulb and burette joined through a connecting arm. The experimental procedure consisted of holding the liquid in the burette at a constant temperature and gradually raising the temperature at which the bulb was maintained to successively higher and higher readings. By knowing the volume of the bulb, and the volume of the liquid in the burette, the calculations described above were possible of attainment.

As a part of this research, the liquid density of trifluoroacetic acid was determined by use of a calibrated dilatometer. The equation expressing the variation of the liquid density with the temperature in the range 30-80° C. was determined by the method of least squares. It was found to be

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As a part of this research, the liquid density of trifluoroacetic acid was determined by use of a calibrated dilatometer. The equation expressing the variation of the liquid density with the temperature in the range 20-30°C. was determined by the method of least squares. It was found

$$\rho = 1.5402 - (2.506 \times 10^{-3})t + (1.863 \times 10^{-7})t^2$$

The conclusions reached as a result of this investigation may be summarized as follows: (1) the strength of the hydrogen bond in trifluoroacetic acid vapor is 7200 ± 250 cal./mole; (2) the order of polymerization of trifluoroacetic acid is no higher than two; (3) there is no appreciable difference in the heats of association of trifluoroacetic acid and acetic acid.

A tentative hypothesis is offered that regardless of the substituent group, the hydrogen bond strengths of all aliphatic carboxylic acids will be essentially the same.

$$Q = 1.5402 - (2.50 \times 10^{-3}) + (1.88 \times 10^{-7}) S$$

The conclusions reached as a result of this investigation may be summarized as follows: (1) the strength of the hydrogen bond in trifluoroacetic acid vapor is 4200 ± 250 cal./mole; (2) the order of polymerization of trifluoroacetic acid is no higher than two; (3) there is no appreciable difference in the heats of association of trifluoroacetic acid and acetic acid.

A tentative hypothesis is offered that regardless of the substituent group, the hydrogen bond strengths of all aliphatic carboxylic acids will be essentially the same.

Table 22

Freezing Point of Trichloroethylene Acid
(No Crystallization)

June 10, 1949
Zero time - 4:25 pm.
Bath Temperature: $-30 \pm 2^{\circ}\text{C}$

Time (minutes)	Battery (scale-cm.)	Heat Point (scale-cm.)	Boiling ($^{\circ}\text{C}$)	Galvanometer Reading (scale-ma.)	Temperature Equivalent ($^{\circ}\text{C}$)
0	34.0	33.0	100	15.0	-18.78
10	31.0	32.0	100	15.0	-18.78
15	31.0	32.0	100	15.0	-18.78
20	31.0	32.0	100	15.0	-18.78
25	31.0	32.0	100	15.0	-18.78
30	31.0	32.0	100	15.0	-18.78
35	31.0	32.0	100	15.0	-18.78
40	31.0	32.0	100	15.0	-18.78
45	31.0	32.0	100	15.0	-18.78
50	31.0	32.0	100	15.0	-18.78
55	31.0	32.0	100	15.0	-18.78
60	31.0	32.0	100	15.0	-18.78
65	31.0	32.0	100	15.0	-18.78
70	31.0	32.0	100	15.0	-18.78
75	31.0	32.0	100	15.0	-18.78
80	31.0	32.0	100	15.0	-18.78
85	31.0	32.0	100	15.0	-18.78
90	31.0	32.0	100	15.0	-18.78
95	31.0	32.0	100	15.0	-18.78
100	31.0	32.0	100	15.0	-18.78

Appendix 1

Time (minutes)	Battery (scale-cm.)	Heat Point (scale-cm.)	Boiling ($^{\circ}\text{C}$)	Galvanometer Reading (scale-ma.)	Temperature Equivalent ($^{\circ}\text{C}$)
0	34.0	33.0	100	15.0	-18.78
10	31.0	32.0	100	15.0	-18.78
20	31.0	32.0	100	15.0	-18.78
30	31.0	32.0	100	15.0	-18.78
40	31.0	32.0	100	15.0	-18.78
50	31.0	32.0	100	15.0	-18.78
60	31.0	32.0	100	15.0	-18.78
70	31.0	32.0	100	15.0	-18.78
80	31.0	32.0	100	15.0	-18.78
90	31.0	32.0	100	15.0	-18.78
100	31.0	32.0	100	15.0	-18.78



1. 11/10/1910



Table 22

Freezing Point of Trifluoroacetic Acid
(No Crystallizations)

June 18, 1948

Zero time: - 4:28 pm.

Bath Temperature: - $20 \pm 2^\circ\text{C}$

Time (minutes)	Battery (scale-cm.)	Rest Point (scale-cm.)	Setting (μV)	Galvanometer Reading (scale-cm.)	Temperature Equivalent ($^\circ\text{C}$)
5	34.0	33.9	132	33.9	—
10	34.0	33.9	232	33.9	—
15	34.0	33.8	308	33.8	—
20	34.0	33.8	366	33.8	—
25	34.0	33.8	424	33.8	—
30	34.0	33.9	465	33.9	-12.26
35	34.0	33.9	494	33.9	-13.04
40	34.0	33.9	519	33.9	-13.71
45	34.0	33.9	540	33.9	-14.29
50	34.0	33.9	553	33.9	-14.63
55	34.0	33.9	561	33.9	-14.84
60	34.0	33.9	570.3	33.9	-15.10
62	34.0	33.9	572.6	33.9	-15.16
65	34.0	33.8	577.2	33.8	-15.28
67	34.0	33.8	580.7	33.8	-15.38
69	34.0	33.8	582.3	33.8	-15.43
formation of crystals					
71	34.0	33.8	577.5	33.8	-15.29
75	34.0	33.8	573	20.5	-15.26
			578	40.8	
80	34.0	33.7	573	22.5	-15.25
			578	42.8	
90	34.0	33.7	573	18.7	-15.26
			578	41.0	

stirrer frozen

Table 23

Freezing Point of Trifluoroacetic Acid
(After Three Crystallizations)

June 18, 1948

Zero Time: 10:15 pm.

Bath Temperature: $-20 \pm 2^{\circ} \text{C}$

Time (minutes)	Battery (scale-cm.)	Rest Point (scale-cm.)		Setting (μV)	Galvanometer Reading (scale-cm.)	Temperature Equivalent ($^{\circ}\text{C}$)
		Before	After			
5	33.0	33.0	33.0	above 0°C	—	—
10	33.0	33.0	33.0	" "	—	—
15	33.5	33.6	33.6	0	33.6	—
20	33.5	33.6	33.6	153	33.6	—
25	33.5	33.6	33.6	281	33.6	—
30	33.5	33.5	33.4	368	33.5	—
35	33.5	33.4	33.4	439	33.4	—
40	33.5	33.4	33.4	492.5	33.4	-13.00
45	33.5	33.4	33.4	529.5	33.4	-14.00
50	33.5	33.4	33.4	550.5	33.4	-14.56
55	33.5	33.4	33.4	564.5	33.4	-14.94
60	33.5	33.4	33.4	576.4	33.4	-15.26
62	33.5	33.4	33.4	579.6	33.4	-15.35
formation of crystals						
64	33.5	33.4	33.4	576.8	33.4	-15.27
67	33.5	33.4	33.4	573	25.0	-15.22
				578	46.0	
75	33.5	33.4	33.4	573	28.5	-15.20
				578	49.5	
85	33.5	33.4	33.4	573	28.4	-15.20
				578	48.8	
95	33.5	33.4	33.4	573	28.3	-15.20
				578	49.0	
105	33.5	33.4	33.4	573	28.5	-15.20
				578	49.1	

stirrer frozen

Table 24

Freezing Point of Trifluoroacetic Acid
(After Six Crystallizations)

June 19, 1948

Zero Time: 2:30 am.

Bath Temperature: $-20 \pm 2^{\circ}\text{C}$

Time (minutes)	Battery (scale-cm.)	Rest Point (scale-cm.)		Setting (μV)	Galvanometer Reading (scale-cm.)	Temperature Equivalent ($^{\circ}\text{C}$)
		Before	After			
5	33.5	33.5	33.5	above 0°C	—	—
10	33.5	33.5	33.5	" "	—	—
15	33.5	33.5	33.5	120	33.5	—
20	33.5	33.5	33.5	237	33.5	—
25	33.5	33.5	33.5	331	33.5	—
30	33.5	33.5	33.5	412	33.5	—
35	33.5	33.5	33.5	473.8	33.5	-12.50
40	33.5	33.5	33.5	503.8	33.5	-13.30
45	33.5	33.5	33.5	529.3	33.5	-13.99
50	33.5	33.5	33.5	550.8	33.5	-14.57
55	33.5	33.5	33.5	568.5	33.5	-15.05
60	33.5	33.5	33.5	576.2	33.5	-15.25
formation of crystals						
62	33.5	33.5	33.5	574.3	33.5	-15.20
65	33.5	33.5	33.5	573	28.4	-15.20
				578	48.2	
75	33.5	33.5	33.5	573	30.5	-15.18
				578	51.5	
85	33.5	33.5	33.5	573	25.0	-15.22
				578	45.5	
95	33.5	33.5	33.5	573	28.5	-15.20
				578	49.0	
105	33.5	33.5	33.5	573	28.8	-15.20
				578	49.0	
115	33.5	33.5	33.5	573	27.8	-15.21
				578	48.2	

stirrer frozen

Table 25

Freezing Point of Trifluoroacetic Acid
(After Eight Crystallizations)

June 19, 1948

Zero Time: 6:00 a.m.

Bath Temperature: $-20 \pm 2^\circ \text{C}$

Time (minutes)	Battery (scale-cm.)	Rest Point (scale-cm.)		Setting (μv)	Galvanometer Reading (scale-cm.)	Temperature Equivalent ($^\circ\text{C}$)
		Before	After			
5	33.5	33.5	33.5	above 0°C	—	—
10	33.5	33.5	33.5	" "	—	—
15	33.5	33.5	33.5	48	33.5	—
20	33.5	33.5	33.5	170	33.5	—
25	33.5	33.5	33.5	274	33.5	—
30	33.5	33.5	33.5	359	33.5	—
35	33.5	33.5	33.5	444	33.5	—
40	33.5	33.5	33.5	492.7	33.5	-13.00
45	33.5	33.5	33.5	530.2	33.5	-14.01
50	33.5	33.5	33.5	551.0	33.5	-14.57
55	33.5	33.5	33.5	564.5	33.5	-14.94
60	33.5	33.5	33.5	574.1	33.5	-15.20
62	33.5	33.5	33.5	576.7	33.5	-15.27
formation of crystals						
65	33.5	33.5	33.5	574.4	33.5	-15.20
70	33.5	33.5	33.5	573	28.4	-15.20
				578	49.0	
80	33.5	33.5	33.5	573	27.9	-15.19
				578	48.2	
90	33.5	33.5	33.5	573	28.8	-15.20
				578	49.9	
100	33.5	33.5	33.5	573	30.4	-15.18
				578	51.0	
110	33.5	33.5	33.5	573	28.5	-15.20
				578	49.0	
120	33.5	33.5	33.5	573	29.0	-15.20
				578	49.5	

stirrer frozen

Table 26

Calibration of Dilatometer:
Uniformity of Capillary Bore

October 23, 1948

Upper Reading	Lower Reading	Length	Average
66.305	56.665	9.640	9.637
66.300	56.665	9.635	
66.300	56.665	9.635	
63.300	53.680	9.620	9.625
63.300	53.675	9.625	
63.300	53.670	9.630	
60.390	50.775	9.615	9.623
60.390	50.760	9.630	
60.370	50.745	9.625	
60.370	50.750	9.620	
57.240	47.605	9.635	9.630
57.210	47.590	9.620	
57.230	47.600	9.635	
54.115	44.480	9.635	9.638
54.120	44.480	9.640	
54.120	44.480	9.640	
51.440	41.795	9.645	9.642
51.425	41.785	9.640	
51.420	41.780	9.640	
50.095	40.480	9.615	9.637
50.105	40.465	9.640	
50.100	40.465	9.635	
50.100	40.460	9.640	

Overall Average: 9.633 0.01 cm.

Calibration of Dilatometer:
 Uniformity of Capillary Bore

Table 28

October 25, 1948

Upper Reading	Lower Reading	Length	Average
55.305	55.665	9.640	9.637
55.300	55.665	9.635	
55.300	55.665	9.635	
55.300	55.680	9.630	9.635
55.300	55.675	9.635	
55.300	55.670	9.630	
50.390	50.775	9.615	9.623
50.390	50.780	9.630	
50.390	50.775	9.635	
50.390	50.780	9.630	
57.240	47.605	9.635	9.630
57.210	47.590	9.630	
57.230	47.600	9.635	
54.115	44.480	9.635	9.638
54.120	44.480	9.640	
54.120	44.480	9.640	
51.440	41.795	9.645	9.645
51.435	41.795	9.640	
51.430	41.790	9.640	
50.095	40.480	9.615	9.637
50.105	40.485	9.640	
50.100	40.485	9.635	
50.100	40.480	9.640	

Overall Average: 9.635 0.01 cm.

Table 27

Calibration of Dilatometer:
Volume of Capillary

October 26, 1948

Upper Reading (cm.)	Lower Reading (cm.)	Length (cm.)	Average (cm.)
Distance Between Scratches:			
99.710	72.465	27.245	27.242
99.710	72.470	27.240	
99.705	72.465	27.240	
Length of Mercury Column:			
99.475	72.740	26.735	26.738
99.470 (a)	72.760* (b)	26.710	
99.500	72.760	26.740	
99.500	72.760	26.740	

Temperature = 24.2° C.

*This reading was discarded because the column of mercury slipped in the capillary between reading (a) and (b).

weighing bottle + Hg: 20.1874 gm.
weighing bottle (empty): 17.4905 gm.
Hg : 2.6969 gm.
Density of Hg @ 24.2°: 13.5359 gm./cc.

$$\text{Volume/cm.} = \frac{2.6969}{(13.5359)(26.738)}$$

$$= 7.4514 \times 10^{-3} \text{ cc./cm.}$$

$$\text{Volume between scratches} = (7.4514 \times 10^{-3})(27.242)$$

$$= 0.2030 \text{ cc.}$$

The value for the cubical coefficient of expansion of glass is obtained from: Kelly, J., and Rao, W. W., "Physical Chemical Methods", Vol. 1, D. van Nostrand Co., New York, N. Y., 1939, p. 27.

Table 27

Calibration of Dilatometer:
Volume of Capillary

October 26, 1948

Upper Reading (cm.)	Lower Reading (cm.)	Length (cm.)	Average (cm.)
Distance Between Scratches:			
99.710	72.465	27.245	27.242
99.710	72.470	27.240	
99.705	72.465	27.240	
Length of Mercury Column:			
99.475	72.740	26.735	26.738
99.470 (a)	72.750* (b)	26.710	
99.500	72.750	26.740	
99.500	72.750	26.740	

Temperature = 24.3° C.

*This reading was discarded because the column of mercury slipped in the capillary between reading (a) and (b).

Density of Hg @ 24.3°: 13.5359 gm/cc.
H₂: 0.0009 gm.
weighing bottle (empty): 17.4905 gm.
weighing bottle + Hg: 20.1874 gm.

$$\text{Volume/cm.} = \frac{2.6969}{(13.5359) - (0.0009)}$$

$$= 7.4514 \times 10^{-3} \text{ cc./cm.}$$

$$\text{Volume between scratches} = (7.4514 \times 10^{-3})(27.242)$$

$$= 0.2030 \text{ cc.}$$

Table 28

Calibration of Dilatometer:
Volume of Bulb

October 26, 1948

Temperature (°C.)	Scratch (cm.)	Meniscus (cm.)	Length of Water Column above Scratch (cm.)	Length of Water Column above Scratch (average)
27.6	74.275	82.720	8.445	
27.8	74.280	82.725	8.445	
27.8	74.275	82.720	8.445	8.446
27.8	74.275	82.725	8.450	

dilatometer + water: 40.5214 gm.

dilatometer (empty): 38.8090 gm.

water: 1.7124 gm.

Density of water @ 27.8°: 0.99629 gm./cc.

Volume/cm. @ 24.2° C. = 7.4514×10^{-3} cc./cm.Volume/cm. @ 27.8° C. = (7.4514×10^{-3})

$$\left[1 + (3.6)(25 \times 10^{-6}) \right]^* \\ = 7.452 \times 10^{-3} \text{ cc./cm.}$$

$$\text{Volume (total)} = \frac{1.7124}{0.99629} = 1.7187 \text{ cc.}$$

Volume of Bulb to scratch @ 27.8° C.

$$= 1.7187 - (8.446)(7.452 \times 10^{-3})$$

$$= 1.6558 \text{ cc.}$$

*

The value for the cubical coefficient of expansion of glass is obtained from: Reilly, J., and Rae, W. N., "Physico-Chemical Methods", Vol. I, D. van Nostrand Co., New York, N. Y., 1939, p. 37.

* The value for the cubical coefficient of expansion of glass is obtained from: Reilly, J., and Rees, W. W., "Physical Chemical Methods", Vol. I, D. van Nostrand Co., New York, N. Y., 1939, p. 37.

$$= 1.8558 \text{ cc.}$$

$$= 1.7187 - (8.446)(7.452 \times 10^{-3})$$

$$\text{Volume of bulb to scratch @ } 27.8^{\circ} \text{ C.} = \frac{1.7184}{0.99829}$$

$$= 1.7187 \text{ cc.}$$

$$= 7.452 \times 10^{-3} \text{ cc./cm.}$$

$$\Delta V = V_2 - V_1 = (7.452 \times 10^{-3}) - (7.4514 \times 10^{-3})$$

$$\text{Volume/cm. @ } 24.2^{\circ} \text{ C.} = 7.4514 \times 10^{-3} \text{ cc./cm.}$$

$$\text{Density of water @ } 27.8^{\circ} \text{ C.} = 0.99829 \text{ gm./cc.}$$

$$\text{water: } 1.7184 \text{ gm.}$$

$$\text{dilatometer (empty): } 38.9090 \text{ gm.}$$

$$\text{dilatometer + water: } 40.6274 \text{ gm.}$$

Temperature (°C.)	Scratch (cm.)	Meniscus (cm.)	Length of Water Column above Scratch (cm.)	Length of Water Column above Scratch (average)
27.8	74.275	82.720	8.445	8.446
27.8	74.280	82.725	8.445	
27.8	74.275	82.720	8.445	
27.8	74.275	82.725	8.450	

October 26, 1948

Calibration of Dilatometer;
Volume of Bulb

Table 28

Table 30

Calibration of the Burette Tube:
Uniformity of Bore

With tube full of water:

Position of Mercury Slug (against inch scale)	Length of Mercury Slug (Ave.) (cm.)
$1\frac{1}{2}$ - $4\frac{1}{2}$	8.248
5 - 7	8.250
6 - 9	8.253
$9\frac{1}{2}$ - $13\frac{1}{2}$	8.265
12 - 15	8.263
14 - 17	8.269
17 - 20	8.253
$19\frac{1}{2}$ - $22\frac{1}{2}$	8.270
$20\frac{1}{2}$ - $23\frac{1}{2}$	8.268

With tube half full Average: 8.259 ± 0.01 cm.

Wt. tube + water: 14.1546 gm.
Wt. tube (empty): 12.5049 gm.
Wt. water: 1.6497 gm.

Height of Scratch (cm.)	Height of Meniscus (cm.)	Difference (cm.)	Average (cm.)
38.170	8.465	30.705	
38.125	8.435	30.700	
38.185	8.465	30.700	
38.170	8.465	30.705	
38.170	8.465	30.705	30.703
38.170	8.435	30.705	± 0.002
38.185	8.465	30.700	
38.170	8.445	30.705	
38.170	8.470	30.700	
38.125	8.425	30.700	

Temperature = 25.65°C .

Volume of burette (in cc./cm. tube length)
at 25.65°C . = 5.0602×10^{-3} cc./cm.

Volume of burette to the reference mark
at 24.85°C . = 2.2343 cc.

Table 30

Calibration of the Burette Tube:
Uniformity of Bore

Position of Mercury Plug (against inch scale)	Length of Mercury Plug (Ave.) (cm.)
1 1/2 - 4 1/2	8.248
5 - 7	8.250
8 - 9	8.252
9 1/2 - 12 1/2	8.255
12 - 15	8.257
14 - 17	8.259
17 - 20	8.262
19 1/2 - 22 1/2	8.270
20 1/2 - 23 1/2	8.268

Average: 8.259 ± 0.01 cm.

Table 31

Calibration of Burette: Volume

With tube full of water:

Wt. tube + water: 15.8416 gm.
 Wt. tube (empty): 12.6849 gm.
 Wt. water: 3.1567 gm.

Height of Meniscus (cm.)	Height of Scratch (cm.)	Difference (cm.)	Average (cm.)
40.270	37.765	2.505	
40.265	37.770	2.495	
40.265	37.770	2.485	
40.270	37.765	2.505	
40.270	37.770	2.500	
40.270	37.765	2.505	
40.260	37.760	2.500	2.501
40.265	37.765	2.500	±0.005
40.265	37.760	2.505	
40.265	37.760	2.505	
40.260	37.755	2.505	
40.255	37.755	2.500	

Temperature = 23.82°C.

With tube half full of water:

Wt. tube + water: 14.1546 gm.
 Wt. tube (empty): 12.6849 gm.
 Wt. water: 1.4697 gm.

Height of Scratch (cm.)	Height of Meniscus (cm.)	Difference (cm.)	Average (cm.)
38.170	8.465	30.705	
38.165	8.465	30.700	
38.165	8.465	30.700	
38.170	8.465	30.705	
38.170	8.465	30.705	30.703
38.170	8.465	30.705	±0.002
38.165	8.465	30.700	
38.170	8.465	30.705	
38.170	8.470	30.700	
38.165	8.465	30.700	

Temperature = 25.65°C.

Volume of burette (in cc./cm. tube length)
 at 25.65 C. = 5.0803×10^{-2} cc./cm.

Volume of burette to the reference mark
 at 24.82°C. = 2.9845 cc.

Table 31
Calibration of Burette: Volume

With tube full of water:

Wt. tube + water: 12.8416 gm.
Wt. tube (empty): 12.8849 gm.
Wt. water: 3.1887 gm.

Meniscus (cm.)	Height of Scratch (cm.)	Difference (cm.)	Average (cm.)
40.270	37.785	2.505	2.501 ±0.005
40.285	37.770	2.515	
40.298	37.770	2.528	
40.270	37.765	2.505	
40.270	37.770	2.500	
40.270	37.765	2.505	
40.280	37.760	2.520	
40.285	37.765	2.520	
40.288	37.760	2.528	
40.288	37.760	2.528	
40.280	37.755	2.525	
40.285	37.755	2.530	

Temperature = 23.820C.

With tube half full of water:

Wt. tube + water: 14.1546 gm.
Wt. tube (empty): 12.8849 gm.
Wt. water: 1.4897 gm.

Meniscus (cm.)	Height of Scratch (cm.)	Difference (cm.)	Average (cm.)
38.170	8.465	30.705	30.703 ±0.005
38.155	8.465	30.700	
38.168	8.465	30.700	
38.170	8.465	30.705	
38.170	8.465	30.705	
38.170	8.465	30.705	
38.165	8.465	30.700	
38.165	8.465	30.705	
38.170	8.465	30.700	
38.170	8.465	30.700	
38.165	8.465	30.700	
38.165	8.465	30.700	

Temperature = 25.650C.

Volume of burette (in cc./cm. tube length)
at 25.65 C. = 5.0803x10⁻⁵ cc./cm.

Volume of burette to the reference mark
at 24.820 C. = 2.9845 cc.

Table 32

Calibration of the Vapor Density Bulb

wt. bulb + water: 341.058 gm.

wt. bulb (empty): 88.572 gm.

wt. water: 252.486 gm.

Temperature = 25.67° C.Volume of bulb at 25.67° C. = 253.274 cc.

Table 33

Calibration of the Connecting Arm

wt. weighing bottle + mercury slug: 88.7235 gm.

wt. weighing bottle (empty) : 17.4908 gm.

wt. mercury slug : 71.2327 gm.

Temperature = 22.2° C.Volume of connecting arm at 22.2° C. = 5.261 cc.

Table 34

Weight of Sample Used in Vapor Density Measurements

wt. sample bulb + sample: 32.9237 gm.

wt. sample bulb (empty) : 28.9369 gm.

wt. sample : 3.0868 gm.

Table 32

Calibration of the Vapor Density Bulb

wt. bulb + water:	341.088 gm.
wt. bulb (empty):	<u>88.572 gm.</u>
wt. water:	252.486 gm.
Temperature =	25.67° C.
Volume of bulb at 25.67° C. =	252.274 cc.

Table 33

Calibration of the Connecting Arm

wt. weighing bottle + mercury slug:	88.7235 gm.
wt. weighing bottle (empty) :	<u>17.4908 gm.</u>
wt. mercury slug :	71.2327 gm.
Temperature =	22.2° C.
Volume of connecting arm at 22.2° C. =	5.261 cc.

Table 34

Weight of Sample Used in Vapor Density Measurements

wt. sample bulb + sample:	32.9237 gm.
wt. sample bulb (empty) :	<u>29.9362 gm.</u>
wt. sample :	3.0868 gm.

Table 35

Run 1 - Vapor Density of Trifluoroacetic Acid
(180 mm. isobar)

December 6, 1948

Zero Time: 10.15 a.m.

Time	Bat- teries (Scale- cm.)	Rest Point (scale-cm.)	Thermostat "A"		Thermostat "B"		Average Tempera- ture of connect- ing Arm (°C.)	Cathetometer Reading (cm.)			
			Poten- tio- meter Set- ting (μ v)	Gal- vanó- meter Read- ing (scale- cm.) (°C.)	Poten- tio- meter Set- ting (μ v)	Gal- vanó- meter Read- ing (Scale- cm.) (°C.)					
Hrs. Min.		Before	After					scratch: 56.120			
0 00	37.0	36.7	36.7	2050	35.0	50.51	1421	33.3	35.58	181	32.870
				2055	48.5		1426	46.5			
0 10	37.0	36.7	36.7	2050	33.5	50.53	1421	30.2	35.61	181	32.870
				2055	46.3		1426	43.5			
0 20	37.0	36.7	36.7	2050	30.3	50.55	1421	31.0	35.60	181	32.875
				2055	43.7		1426	44.2			
scratch: 56.125											
scratch: 56.110											
2 55	36.5	36.7	36.7	2488	33.5	60.68	1421	35.0	35.56	181	33.330
				2493	43.3		1426	48.3			
3 05	36.5	36.7	36.7	2488	35.5	60.66	1421	35.3	35.56	181	33.335
				2493	46.1		1426	47.5			
3 15	36.5	36.7	36.7	2488	32.0	60.69	1421	34.2	35.57	181	33.330
				2493	43.2		1426	47.5			
scratch: 56.120											

Table 35
(continued)

Time	Bat- teries (Scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Potentiometer Set- ting (μ V) (scale -cm.) (°C.)	Thermostat "B" Potentiometer Set- ting (μ V) (Scale T -cm.) (°C.)	Average Cathetometer Temperature of connecting Arm (°C.)
Hrs. Min.	Before	After			scratch: 56.110
11 00	38.0	37.9	37.9	37.9	181
			5755	33.5	131.28
			5760	44.3	1426
11 10	38.0	37.9	37.9	37.9	181
			5755	33.2	131.29
			5760	44.5	1426
11 20	38.0	37.9	37.9	37.9	181
			5755	34.7	131.28
			5760	43.4	1426
scratch: 56.115					
11 50	38.0	37.8	37.8	37.8	181
			6252	32.8	141.43
			6257	40.0	1426
12 00	38.0	37.8	37.8	37.8	181
			6252	35.0	141.38
			6257	45.2	1426
12 10	38.0	37.8	37.8	37.8	181
			6252	30.0	141.44
			6257	38.9	1426
scratch: 56.110					
12 45	38.5	38.4	38.4	38.4	181
			6868	31.3	153.80
			6873	39.0	1426
12 55	38.5	38.4	38.4	38.4	181
			6868	34.5	153.76
			6873	42.0	1426
13 05	38.5	38.4	38.4	38.4	181
			6868	34.5	153.76
			6873	42.0	1426
scratch: 56.110					

End of Run 1
Thermostat "A" controls to $\pm 0.02^\circ \text{C}$.
Thermostat "B" controls to $\pm 0.02^\circ \text{C}$.

Table 36

Run 2 - Vapor Density of Trifluoroacetic Acid
(247 mm. isobar)

November 19, 1948

Zero Time: 11:15 a.m.

Time	Bat- teries (Scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Poten-Gal- tio- vano- meter Set- Read- ting ing (scale T -cm.) (°C.)	(μV)	Thermostat "B" Poten- Gal- tio- vano- meter Set- Read- ting ing (scale T -cm.) (°C.)	Average Cathetometer Tempera- Reading ture of connect- ing Arm (cm.)					
Hrs.Min.	Before	After									
0 00	39.0	38.8	38.8	2295 2300	30.0 41.0	56.28 56.28	1728 1733	34.1 46.5	42.93 42.93	175 175	scratch: 56.145 31.035
1 50	38.0	38.0	38.1	2295 2300	30.0 41.9	56.27 56.27	1725 1730	33.0 46.5	42.86 42.86	175 175	31.050
2 00	38.0	38.2	38.2	2295 2300	29.8 42.3	56.27 56.27	1725 1730	30.5 43.9	42.89 42.89	175 175	31.050
2 10	38.0	38.0	37.7	2295 2300	29.5 43.4	56.26 56.26	1725 1730	32.2 45.5	42.87 42.87	175 175	31.050 scratch: 56.145
3 35	37.5	37.4	37.4	2803 2808	33.5 47.8	67.85 67.85	1725 1730	31.3 43.8	42.88 42.88	175 175	scratch: 56.145 31.690
3 50	37.5	37.3	37.0	2803 2808	33.2 46.0	67.85 67.85	1725 1730	19.4 30.4	42.97* 42.97*	175 175	31.695
4 00	37.0	37.0	36.7	2803 2808	33.0 46.4	67.85 67.85	1725 1730	19.0 31.0	42.97* 42.97*	175 175	31.695 scratch: 56.140

*Light source directly in back of thermocouple junction caused local overheating.

Table 36
(continued)

Time	Bat- teries (Scale -cm.)	Rest Point	Thermostat "A"		Thermostat "B"		Average Tempera- ture of connect- ing Arm (°C.)	Cathetometer Reading (cm.)
Hrs.Min.	Before	After	Poten- tio- meter Set- ting (μv)	Gal- vano- meter Read- ing (scale -cm.)	Poten- tio- meter Set- ting (μv)	Gal- vano- meter Read- ing (scale -cm.)	(°C.)	
6 55	36.5	35.9	3233	33.3	77.49	1725	27.8	scratch: 56.140
			3238	46.5		1730	41.3	32.295
7 05	36.5	36.8	3233	30.3	77.52	1725	32.5	32.295
			3238	43.5		1730	44.0	
7 15	37.0	36.7	3233	31.0	77.52	1725	32.0	32.295
			3238	44.2		1730	46.0	scratch: 56.125
8 45	36.5	36.2	3706	31.1	87.95	1725	32.5	scratch: 56.130
			3711	43.6		1730	45.3	32.810
8 55	36.5	36.2	3706	31.6	87.95	1725	32.5	32.815
			3711	43.5		1730	45.0	
9 05	36.5	36.2	3706	33.7	87.94	1725	33.0	32.835
			3711	44.2		1730	45.0	
9 15	36.5	36.2	3706	35.0	87.92	1725	33.0	32.840
			3711	45.5		1730	45.3	scratch: 56.140
10 45	36.0	35.8	4173	32.8	98.07	1725	32.5	scratch: 56.145
			4178	44.2		1730	44.5	33.355
10 55	36.0	35.8	4173	31.0	98.09	1725	32.5	33.350
			4178	42.7		1730	44.0	
11 05	36.0	35.7	4173	31.2	98.08	1725	32.4	33.355
			4178	43.0		1730	44.7	scratch: 56.145

Table 36
(continued)

Time	Bat- teries (Scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Poten- Gal- tio- vano- meter Set- Read- ting (°C.) (scale -cm.)	Thermostat "B" Poten- Gal- tio- vano- meter Set- Read- ting (°C.) (scale -cm.)	Average Tempera- ture of connect- ing Arm (°C.)	Cathetometer Reading (cm.)				
Hrs.Min.	Before	After								
5 10	35.5	35.5	35.4	5588 5593	31.0 39.8	127.86 1723	30.5 42.5	42.82	175	scratch: 56.145
5 20	35.5	35.2	35.1	5588 5593	28.6 37.0	127.90 1723	31.8 42.8	42.81	175	34.575
5 30	35.0	35.1	35.1	5588 5593	31.5 39.0	127.86 1723	29.0 43.8	42.82	175	34.575
										scratch: 56.135
7 00	34.5	34.4	34.4	6092 6097	30.3 38.5	138.16 1723	26.0 39.7	42.84	175	scratch: 56.140
7 10	34.5	34.4	34.4	6092 6097	29.1 41.6	138.16 1723	28.5 42.0	42.82	175	34.795
7 20	34.5	34.2	34.2	6092 6097	32.5 42.0	138.13 1723	28.0 40.0	42.82	175	34.805
										scratch: 56.150
9 10	34.0	34.0	34.0	6718 6723	29.0 39.0	150.77 1723	26.0 38.4	42.84	175	scratch: 56.150
9 20	34.0	34.0	34.0	6718 6723	28.4 37.0	150.79 1723	22.5 35.2	42.86	175	35.040
9 30	34.0	34.0	34.0	6718 6723	31.2 40.0	150.76 1723	28.4 41.4	42.82	175	35.040
										scratch: 56.145

End of Run 2
Thermostat "A" controls to $\pm 0.02^{\circ}C.$
Thermostat "B" controls to $\pm 0.04^{\circ}C.$

Table 37

Run 3 - Vapor Density of Trifluoroacetic Acid
(343 mm. isobar)

November 26, 1948

Zero Time: 1:00 p.m.

Time	Bat- teries (scale -cm.)	Rest Point (scale) -cm.)	Poten- Gal- tio- vano- meter Set- ting	(μV)	Read- ing (scale -cm.)	T (°C.)	Poten- Gal- tio- vano- meter Set- ting	(μV)	Read- ing (scale -cm.)	T (°C.)	connect- ing Arm (°C.)	Average Cathetometer Tempera- Reading ture of connect- ing Arm (cm.)
Hrs. Min.	Before After											
0 05	34.0	34.3	34.3	2703 2708	29.3 40.0	65.60	2060 2065	29.5 40.7	50.74	168	scratch: 56.145 28.595	
0 15	34.0	34.3	34.2	2703 2708	27.8 39.5	65.61	2060 2065	29.5 41.2	50.74	168	28.615	
0 25	34.0	34.2	34.2	2703 2708	22.5 35.3	65.65	2060 2065	30.0 40.5	50.74	168	28.615	
0 35	34.0	34.2	34.1	2703 2708	22.5 35.5	65.65	2060 2065	27.5 39.0	50.76	168	28.620	
											scratch: 56.140	

November 28, 1948

Zero Time: 9:00 a.m.

0	10	34.0	33.6	33.8	3201 3206	29.0 40.3	76.80 2060 2065	27.0 38.5	50.76	168	scratch: 56.150 29.730
0	20	34.0	33.7	33.7	3201 3206	26.3 39.2	76.82 2062 2067	30.3 43.8	50.77	168	29.725
00	30	34.0	33.7	33.6	3201 3206	22.0 34.2	76.86 2062 2067	30.3 42.0	50.77	168	29.730
scratch: 56.150											

Table 37
(continued)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A"		Thermostat "B"		Average Cathetometer				
Hrs.Min.		Before	After	Poten- tio- meter Set- ting (μV)	Gal- vano- meter Read- ing (scale -cm.)	Poten- tio- meter Set- ting (μV)	Gal- vano- meter Read- ing (scale -cm.)	Tempera- ture of connect- ing Arm ($^{\circ}C.$)	Reading (cm.)		
<hr/>											
1 45	38.0	38.2	38.2	3653	33.5	86.81	2062	33.5	50.78	168	scratch: 56.150
				3658	42.5		2067	47.0			30.485
1 55	38.0	38.2	38.2	3653	35.5	86.77	2062	32.0	50.79	168	30.490
				3658	48.5		2067	44.5			
2 05	38.0	38.3	38.3	3653	34.3	86.79	2062	34.2	50.78	168	30.490
				3658	44.2		2067	46.5			scratch: 56.145
<hr/>											
4 20	38.5	38.5	38.5	4127	33.3	97.09	2062	36.3	50.76	168	scratch: 56.145
				4132	46.5		2067	48.5			31.260
4 30	38.5	38.7	38.7	4127	37.5	97.06	2062	36.3	50.76	168	31.255
				4132	49.9		2067	47.5			
4 40	38.5	38.8	38.8	4127	35.5	97.08	2062	37.4	50.75	168	31.265
				4132	48.5		2067	47.8			scratch: 56.150
<hr/>											
6 10	41.0	41.2	41.4	4611	39.5	107.42	2060	38.3	50.72	168	scratch: 56.140
				4616	52.2		2065	50.0			31.940
6 20	41.5	41.4	42.0	4611	40.2	107.42	2060	39.2	50.72	168	31.945
				4616	52.0		2065	52.6			
6 30	42.0	41.8	41.8	4611	40.5	107.42	2060	38.7	50.72	168	31.945
				4616	55.0		2065	51.5			scratch: 56.145

Table 37
(continued)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A"		Thermostat "B"		Average Cathetometer	
Hrs.Min.	Before	After	Poten- tio- meter Set- ting (μ v) (scale -cm.)	Gal- vano- meter Read- ing ($^{\circ}$ C.) (scale -cm.)	Poten- tio- meter Set- ting (μ v) (scale -cm.)	Gal- vano- meter Read- ing ($^{\circ}$ C.) (scale -cm.)	Tempera- ture of connect- ing Arm ($^{\circ}$ C.)	Reading (cm.)
1 40	42.0	41.8 41.7	6066 6071	34.5 137.69 42.0	2062 2067	34.5 50.80 46.7	168	scratch: 56.150 33.575
1 50	42.0	41.7 41.6	6069 6074	35.0 137.73 42.8	2062 2067	35.9 50.78 49.3	168	33.580
2 00	41.5	41.6 41.5	6066 6071	38.0 137.65 44.0	2062 2067	36.5 50.78 49.4	168	33.590
scratch: 56.145								
3 45	41.5	41.6 41.6	6747 6752	37.2 151.35 46.3	2062 2067	37.0 50.77 49.0	168	scratch: 56.145 33.995
3 55	41.5	41.5 41.5	6747 6752	37.3 151.35 46.0	2062 2067	36.7 50.78 49.5	168	34.000
4 05	41.5	41.5 41.5	6747 6752	36.5 151.35 45.3	2062 2067	36.5 50.78 49.5	168	34.000
scratch: 56.145								

End of Run 3

Thermostat "A" controls to $\pm 0.02^{\circ}$ C.Thermostat "B" controls to $\pm 0.03^{\circ}$ C.

Table 38
(concluded)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat Poten- tio- meter Set- ting (μV)	Thermostat "A" Gal- vano- meter Read- ing (scale -cm.)	T (°C.)	Thermostat "B" Poten- tio- meter Set- ting (μV)	Thermostat "B" Gal- vano- meter Read- ing (scale -cm.)	T (°C.)	Average Tempera- ture of connect- ing Arm (°C.)	Cathetometer Reading (cm.)
Hrs.Min.	Before	After								scrat
18 00	44.0	44.0	43.9	6961	40.4	155.60	2398	35.5	58.58	172
				6966	48.9		2403	50.8		scratch: 56.120
18 10	44.0	43.9	43.9	6961	38.9	155.61	2398	34.0	58.59	172
				6966	48.5		2403	50.0		32.315
18 20	44.0	43.9	43.8	6961	41.0	155.59	2398	34.2	58.60	172
				6966	49.3		2403	48.6		32.320
										scratch: 56.125

End of Run 4

Thermostat "A" controls to $\pm 0.02^{\circ} \text{C.}$ Thermostat "B" controls to $\pm 0.03^{\circ} \text{C.}$

Table 39

Run 5 - Vapor Density of Trifluoroacetic Acid
(605 mm. Isobar)

December 1, 1948

Zero Time: 1:25 p.m.

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Poten- Gal- tio- vano- meter Set- Read- ting (scale -cm.)	Poten- Gal- tio- vano- meter Set- Read- ting (scale -cm.)	Average Cathetometer Temperature of connecting Arm (°C.)	Reading (cm.)
Hrs.Min.	Before	After	(μr)	(μr)	(°C.)	
0 00	41.0	40.7	3260	78.08	65.35	165
			3265			scratch: 56.115
0 10	41.0	40.7	3260	78.10	65.38	165
			3265			22.045
0 20	41.0	40.7	3260	78.07	65.20(?)	165
			3265			22.045
						scratch: 56.115
1 35	41.5	41.3	3703	87.88	65.38	165
			3708			scratch: 56.100
1 45	41.5	41.3	3703	87.87	65.35	165
			3708			23.420
1 55	41.5	41.2	3703	87.90	65.35	165
			3708			23.425
						scratch: 56.110
3 20	41.0	41.0	4164	97.87	65.36	165
			4169			scratch: 56.110
3 30	41.0	41.0	4164	97.91	65.35	165
			4169			24.885
3 40	41.0	41.0	4164	97.88	65.34	165
			4169			24.885
						scratch: 56.110

Table 39
(concluded)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Potentiometer Setting (°C.)	Thermostat "B" Potentiometer Setting (°C.)	Average Cathetometer Temperature of connecting Arm (cm.)						
Hrs.Min.	Before	After	(μV)	(μV)	(°C.)						
9 25	42.0	42.1	42.0	6150	35.5	139.38	2694	35.3	65.33	165	scratch: 56.125
				6155	42.8		2699	51.2			29.315
9 35	42.0	42.0	42.0	6150	34.3	139.39	2694	38.3	65.34	165	29.320
				6155	41.8		2699	52.8			
9 45	42.0	42.0	42.0	6150	29.5	139.38	2694	37.4	65.33	165	29.320
				6155	43.0		2699	54.3			scratch: 56.110
11 15	42.5	42.8	42.8	6777	39.4	151.94	2694	33.7	65.36	165	scratch: 56.110
				6782	47.4		2699	45.0			30.130
11 25	42.5	43.0	43.0	6777	37.5	151.98	2694	35.7	65.33	165	30.135
				6782	44.8		2699	50.4			
11 35	43.0	43.0	43.0	6777	39.1	151.95	2694	32.0	65.36	165	30.135
				6782	47.1		2699	43.4			scratch: 56.115

End of Run 5

Thermostat "A" controls to $\pm 0.02^\circ \text{C}$.Thermostat "B" controls to $\pm 0.04^\circ \text{C}$.

Run 6 - Vapor Density of Trifluoroacetic Acid
(780 mm. Isobar)

December 3, 1948
Zero Time: 9:25 a.m.

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Poten- tio- meter Set- ting	Thermostat "A" Gal- vano- meter Read- ing	Thermostat "A" (scale -cm.)	(μV)	Thermostat "B" Poten- tio- meter Set- ting	Thermostat "B" Gal- vano- meter Read- ing	Thermostat "B" (scale -cm.)	Average Tempera- ture of Connect- ing Arm (°C.)	Cathetometer Reading (cm.)
Hrs.Min.	Before	After									scratch: 56.105
0 00	41.0	40.8	40.8	3630	35.3	86.30	2995	31.5	72.20	180	17.575
				3635	46.4		3000	42.2			
0 10	41.0	40.8	40.8	3630	30.0	86.35	2995	28.0	72.21	180	17.585
				3635	41.5		3000	41.5			
0 20	40.0	40.3	40.1	3630	32.5	86.33	2995	30.0	72.20	180	17.575
				3635	42.6		3000	42.0			
											scratch: 56.085
1 00	39.5	39.3	39.3	3981	38.0	93.91	2997	33.0	72.21	180	scratch: 56.110
				3986	52.3		3002	44.3			19.020
1 10	39.5	39.5	39.5	3980	37.7	93.91	2997	35.0	72.19	180	19.020
				3985	48.0		3002	46.4			
1 20	39.5	39.4	39.4	3980	38.1	93.91	2997	32.3	72.21	180	19.020
				3985	48.5		3002	45.2			scratch: 56.105
3 50	39.5	39.6	39.6	4433	31.0	103.71	2997	34.5	72.20	180	scratch: 56.115
				4438	41.3		3002	45.7			20.940
4 00	39.5	39.5	39.5	4433	30.5	103.71	2997	32.8	72.20	180	20.940
				4438	40.8		3002	48.0			
4 10	39.5	39.5	39.5	4433	30.0	103.71	2997	33.3	72.21	180	20.940
				4438	40.4		3002	43.8			scratch: 56.115

Table 40
(continued)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Potentiometer Set- ting (μ V)	Thermostat "B" Potentiometer Set- ting (μ V)	Average Temperature of Connecting Arm (°C.)	Cathetometer Reading (cm.)
Hrs.Min.	Before	After	Before	After	Temp.	Reading
5 10	39.6	39.6	39.6 4945 4950	114.50 2997 3002	72.18 180	22.670
5 20	39.5	39.7	39.7 4945 4950	114.50 2997 3002	72.18 180	22.670
5 30	39.5	39.7	39.7 4945 4950	114.50 2997 3002	72.18 180	22.670
scratch: 56.105						
6 20	41.5	41.7	41.7 5483 5488	125.73 2995 3000	72.15 180	24.265
6 30	41.5	41.8	41.8 5483 5488	125.77 2995 3000	72.16 180	24.275
6 40	41.5	41.8	41.6 5483 5488	125.74 2995 3000	72.15 180	24.275
scratch: 56.090						
7 35	39.5	39.8	39.8 5991 5996	136.14 2997 3002	72.18 180	25.570
7 45	39.5	39.8	39.8 5991 5996	136.15 2997 3002	72.18 180	25.575
7 55	39.5	39.8	39.8 5991 5996	136.15 2997 3002	72.17 180	25.575
scratch: 56.105						

Table 40
(concluded)

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Potentiometer Set- ting (μV)	Thermostat "A" Potentiometer Set- ting (scale -cm.)	Thermostat "B" Potentiometer Set- ting (μV)	Thermostat "B" Potentiometer Set- ting (scale -cm.)	Average Temperature of connecting Arm ($^{\circ}C.$)	Cathetometer Reading (cm.)
Hrs. Min.	Before	After						scratch: 56.105
9 25	41.5	41.8	41.8	6483 6488	35.0 43.0	146.10 2995	36.5 180	26.660
9 35	41.5	41.8	41.7	6483 6488	40.8 52.0	146.02 2995	36.3 180	26.660
9 45	41.5	41.7	41.7	6483 6488	34.5 45.3	146.08 2995	35.4 180	26.665
scratch: 56.110								
10 15	39.5	39.8	39.7	6922 6927	33.8 44.2	154.84 2995	35.8 180	scratch: 56.115 27.315
10 25	39.5	39.8	39.8	6922 6927	34.0 45.7	154.83 2995	36.7 180	27.315
10 35	39.5	39.8	39.8	6922 6927	33.4 44.0	154.83 2995	36.0 180	27.315
scratch: 56.100								

End of Run 6

Thermostat "A" controls to $\pm 0.02^{\circ} C.$ Thermostat "B" controls to $\pm 0.03^{\circ} C.$

Table 41

Run 7 - Vapor Density of Trifluoroacetic Acid
(951 mm. Isobar)December 4, 1948
Zero Time: 11:15 a.m.

Time	Bat- teries (scale -cm.)	Rest Point (scale -cm.)	Thermostat "A" Poten- Gal- tio- vano- meter Set- Read- ing (scale -cm.)	Thermostat "B" Poten- Gal- tio- vano- meter Set- Read- ing (scale -cm.)	T (°C.)	Average Temp- ature of connect- ing Arm (°C.)	Average Cathetometer Reading (cm.)
Hrs.Min.	Before	After	(μ r)	(μ r)	(°C.)	(°C.)	
0 00	39.0	39.2	3942 3947	34.7 46.8	93.09	77.89	scratch: 56.075 12.470
0 10	39.0	39.2	3942 3947	35.7 45.8	93.09	77.91	12.470
0 20	39.0	39.2	3942 3947	37.0 45.2	93.08	77.92	12.470
							scratch: 56.085
2 00	39.0	39.0	4540 4545	36.0 42.5	105.95	77.92	scratch: 56.075 15.630
2 10	39.0	39.1	4540 4545	31.5 41.0	105.99	77.92	15.630
2 20	39.0	39.0	4540 4545	34.0 43.5	105.96	77.94	15.635
							scratch: 56.085

Before After									
Time	Lat	Long	Alt	Temp	Wind	Humid	Pres	Cloud	Notes
001.00	20.00	100.00	1000	20.0	0.0	100	1010	0.0	
001.01	20.01	100.01	1001	20.1	0.1	100	1011	0.1	
001.02	20.02	100.02	1002	20.2	0.2	100	1012	0.2	
001.03	20.03	100.03	1003	20.3	0.3	100	1013	0.3	
001.04	20.04	100.04	1004	20.4	0.4	100	1014	0.4	
001.05	20.05	100.05	1005	20.5	0.5	100	1015	0.5	
001.06	20.06	100.06	1006	20.6	0.6	100	1016	0.6	
001.07	20.07	100.07	1007	20.7	0.7	100	1017	0.7	
001.08	20.08	100.08	1008	20.8	0.8	100	1018	0.8	
001.09	20.09	100.09	1009	20.9	0.9	100	1019	0.9	
001.10	20.10	100.10	1010	21.0	1.0	100	1020	1.0	
001.11	20.11	100.11	1011	21.1	1.1	100	1021	1.1	
001.12	20.12	100.12	1012	21.2	1.2	100	1022	1.2	
001.13	20.13	100.13	1013	21.3	1.3	100	1023	1.3	
001.14	20.14	100.14	1014	21.4	1.4	100	1024	1.4	
001.15	20.15	100.15	1015	21.5	1.5	100	1025	1.5	
001.16	20.16	100.16	1016	21.6	1.6	100	1026	1.6	
001.17	20.17	100.17	1017	21.7	1.7	100	1027	1.7	
001.18	20.18	100.18	1018	21.8	1.8	100	1028	1.8	
001.19	20.19	100.19	1019	21.9	1.9	100	1029	1.9	
001.20	20.20	100.20	1020	22.0	2.0	100	1030	2.0	
001.21	20.21	100.21	1021	22.1	2.1	100	1031	2.1	
001.22	20.22	100.22	1022	22.2	2.2	100	1032	2.2	
001.23	20.23	100.23	1023	22.3	2.3	100	1033	2.3	
001.24	20.24	100.24	1024	22.4	2.4	100	1034	2.4	
001.25	20.25	100.25	1025	22.5	2.5	100	1035	2.5	
001.26	20.26	100.26	1026	22.6	2.6	100	1036	2.6	
001.27	20.27	100.27	1027	22.7	2.7	100	1037	2.7	
001.28	20.28	100.28	1028	22.8	2.8	100	1038	2.8	
001.29	20.29	100.29	1029	22.9	2.9	100	1039	2.9	
001.30	20.30	100.30	1030	23.0	3.0	100	1040	3.0	
001.31	20.31	100.31	1031	23.1	3.1	100	1041	3.1	
001.32	20.32	100.32	1032	23.2	3.2	100	1042	3.2	
001.33	20.33	100.33	1033	23.3	3.3	100	1043	3.3	
001.34	20.34	100.34	1034	23.4	3.4	100	1044	3.4	
001.35	20.35	100.35	1035	23.5	3.5	100	1045	3.5	
001.36	20.36	100.36	1036	23.6	3.6	100	1046	3.6	
001.37	20.37	100.37	1037	23.7	3.7	100	1047	3.7	
001.38	20.38	100.38	1038	23.8	3.8	100	1048	3.8	
001.39	20.39	100.39	1039	23.9	3.9	100	1049	3.9	
001.40	20.40	100.40	1040	24.0	4.0	100	1050	4.0	
001.41	20.41	100.41	1041	24.1	4.1	100	1051	4.1	
001.42	20.42	100.42	1042	24.2	4.2	100	1052	4.2	
001.43	20.43	100.43	1043	24.3	4.3	100	1053	4.3	
001.44	20.44	100.44	1044	24.4	4.4	100	1054	4.4	
001.45	20.45	100.45	1045	24.5	4.5	100	1055	4.5	
001.46	20.46	100.46	1046	24.6	4.6	100	1056	4.6	
001.47	20.47	100.47	1047	24.7	4.7	100	1057	4.7	
001.48	20.48	100.48	1048	24.8	4.8	100	1058	4.8	
001.49	20.49	100.49	1049	24.9	4.9	100	1059	4.9	
001.50	20.50	100.50	1050	25.0	5.0	100	1060	5.0	
001.51	20.51	100.51	1051	25.1	5.1	100	1061	5.1	
001.52	20.52	100.52	1052	25.2	5.2	100	1062	5.2	
001.53	20.53	100.53	1053	25.3	5.3	100	1063	5.3	
001.54	20.54	100.54	1054	25.4	5.4	100	1064	5.4	
001.55	20.55	100.55	1055	25.5	5.5	100	1065	5.5	
001.56	20.56	100.56	1056	25.6	5.6	100	1066	5.6	
001.57	20.57	100.57	1057	25.7	5.7	100	1067	5.7	
001.58	20.58	100.58	1058	25.8	5.8	100	1068	5.8	
001.59	20.59	100.59	1059	25.9	5.9	100	1069	5.9	
001.60	20.60	100.60	1060	26.0	6.0	100	1070	6.0	
001.61	20.61	100.61	1061	26.1	6.1	100	1071	6.1	
001.62	20.62	100.62	1062	26.2	6.2	100	1072	6.2	
001.63	20.63	100.63	1063	26.3	6.3	100	1073	6.3	
001.64	20.64	100.64	1064	26.4	6.4	100	1074	6.4	
001.65	20.65	100.65	1065	26.5	6.5	100	1075	6.5	
001.66	20.66	100.66	1066	26.6	6.6	100	1076	6.6	
001.67	20.67	100.67	1067	26.7	6.7	100	1077	6.7	
001.68	20.68	100.68	1068	26.8	6.8	100	1078	6.8	
001.69	20.69	100.69	1069	26.9	6.9	100	1079	6.9	
001.70	20.70	100.70	1070	27.0	7.0	100	1080	7.0	
001.71	20.71	100.71	1071	27.1	7.1	100	1081	7.1	
001.72	20.72	100.72	1072	27.2	7.2	100	1082	7.2	
001.73	20.73	100.73	1073	27.3	7.3	100	1083	7.3	
001.74	20.74	100.74	1074	27.4	7.4	100	1084	7.4	
001.75	20.75	100.75	1075	27.5	7.5	100	1085	7.5	
001.76	20.76	100.76	1076	27.6	7.6	100	1086	7.6	
001.77	20.77	100.77	1077	27.7	7.7	100	1087	7.7	
001.78	20.78	100.78	1078	27.8	7.8	100	1088	7.8	
001.79	20.79	100.79	1079	27.9	7.9	100	1089	7.9	
001.80	20.80	100.80	1080	28.0	8.0	100	1090	8.0	
001.81	20.81	100.81	1081	28.1	8.1	100	1091	8.1	
001.82	20.82	100.82	1082	28.2	8.2	100	1092	8.2	
001.83	20.83	100.83	1083	28.3	8.3	100	1093	8.3	
001.84	20.84	100.84	1084	28.4	8.4	100	1094	8.4	
001.85	20.85	100.85	1085	28.5	8.5	100	1095	8.5	
001.86	20.86	100.86	1086	28.6	8.6	100	1096	8.6	
001.87	20.87	100.87	1087	28.7	8.7	100	1097	8.7	
001.88	20.88	100.88	1088	28.8	8.8	100	1098	8.8	
001.89	20.89	100.89	1089	28.9	8.9	100	1099	8.9	
001.90	20.90	100.90	1090	29.0	9.0	100	1100	9.0	
001.91	20.91	100.91	1091	29.1	9.1	100	1101	9.1	
001.92	20.92	100.92	1092	29.2	9.2	100	1102	9.2	
001.93	20.93	100.93	1093	29.3	9.3	100	1103	9.3	
001.94	20.94	100.94	1094	29.4	9.4	100	1104	9.4	
001.95	20.95	100.95	1095	29.5	9.5	100	1105	9.5	
001.96	20.96	100.96	1096	29.6	9.6	100	1106	9.6	
001.97	20.97	100.97	1097	29.7	9.7	100	1107	9.7	
001.98	20.98	100.98	1098	29.8	9.8	100	1108	9.8	
001.99	20.99	100.99	1099	29.9	9.9	100	1109	9.9	
002.00	21.00	101.00	1100	30.0	10.0	100	1110	10.0	

(continued)

Table 41
(concluded)

Time	Batteries (scale -cm.)	Rest Point (scale -cm.)	Thermostat Potentiometer Set-ting	"A" Thermostat Potentiometer Set-ting	Thermostat Potentiometer Set-ting	"B" Thermostat Potentiometer Set-ting	Average Temperature of connecting Arm (°C.)	Cathetometer Reading (cm.)
Hrs.Min.	Before	After	(μ V)	(scale -cm.)	(μ V)	(scale -cm.)		
5 50	39.5	39.5	6507 6512	33.0 45.2	3253 3258	34.0 50.2	178	scratch: 56.110 22.805
6 00	39.5	39.5	6507 6512	37.5 45.0	3253 3258	33.4 44.4	178	22.810
6 10	39.5	39.5	6507 6512	40.8 49.2	3253 3258	36.1 47.4	178	22.810
scratch: 56.110								
6 45	40.0	39.8	6980 6985	34.3 41.3	3253 3258	35.4 48.6	178	scratch: 56.105 23.880
6 55	40.0	39.7	6980 6985	35.5 43.5	3253 3258	34.1 45.2	178	23.885
7 05	40.0	39.7	6980 6985	31.4 39.3	3253 3258	34.3 47.8	178	23.900
scratch: 56.110								

End of Run 7

Thermostat "A" controls to $\pm 0.03^\circ \text{C}$.Thermostat "B" controls to $\pm 0.03^\circ \text{C}$.

Appendix 2

Calibration of the Thermocouples.

During the course of this research, it was necessary to calibrate three copper-constantan thermocouples, one for the purification work on trifluoroacetic acid, the other two for use in the thermostats connected with the vapor density measurements.

Thermocouple TC-B was calibrated at the sublimation temperature of dry ice and at the melting point of mercury. Thermocouples TC-C and TC-D were calibrated at the temperature of boiling water and at the melting point of tin.

Calibration of Thermocouple TC-B. (27)

A coil of manganin wire of approximately 100 ohms resistance was buried in a small Dewar flask beneath a large quantity of very finely powdered dry ice. The leads of the heater coil were connected to a source of current through a rheostat. The hot junction of thermocouple TC-B was imbedded in the dry ice, care being taken that the junction was at least $1\frac{1}{2}$ inches away from the heater. The reference junction was placed in a Dewar filled with a distilled water-distilled water ice mixture. The potentiometer circuit was balanced, and the EMF of the thermocouple was observed. A current of 0.1 ampere in the heater coil was sufficient to maintain a steady stream of gaseous carbon dioxide sweeping out of the Dewar. Increase of the current to 0.25 ampere produced no measureable change in the final equilibrium temperature

Calibration of the Thermocouples.

During the course of this research, it was necessary to calibrate three copper-constantan thermocouples, one for the purification work on trichloroacetic acid, the other two for use in the thermostats connected with the vapor density measurements.

Thermocouple TC-B was calibrated at the sublimation temperature of dry ice and at the melting point of mercury. Thermocouples TC-C and TC-D were calibrated at the temperature of boiling water and at the melting point of tin.

Calibration of Thermocouple TC-B. (SV)

A coil of manganin wire of approximately 100 ohms resistance was buried in a small Dewar flask beneath a large quantity of very finely powdered dry ice. The leads of the heater coil were connected to a source of current through a rheostat. The hot junction of thermocouple TC-B was imbedded in the dry ice, care being taken that the junction was at least 1 1/2 inches away from the heater. The reference junction was placed in a Dewar filled with a distilled water-distilled water ice mixture. The potentiometer circuit was balanced, and the EMF of the thermocouple was observed. A current of 0.1 amperes in the heater coil was sufficient to maintain a steady stream of gaseous carbon dioxide sweeping out of the Dewar. Increase of the current to 0.25 amperes produced no measurable change in the final equilibrium temperature.

attained by the subliming carbon dioxide. Observations were taken until a steady value of the thermocouple output was observed. The barometric pressure was read at intervals. The data are presented in Table 42.

The hot junction of the thermocouple was mounted in a test tube containing about 50 cc. of mercury (Howe and French, triple distilled). The test tube was fitted with an outer jacket, the assembly was immersed in a dry ice-trichloroethylene bath at -50°C. and EMF readings were taken. After the mercury was completely frozen, the cold bath was removed and the assembly was permitted to warm up. During the warming process, EMF readings were taken. These data are presented in Tables 43-44.

The barometric pressure was corrected for temperature effects by use of the equation

$$p = \frac{1 + (1.84 \times 10^{-5})(t^{\circ}\text{C.})}{1 + (1.818 \times 10^{-4})(t^{\circ}\text{C.})} \times p_{\text{obs.}}$$

The sublimation temperature of solid carbon dioxide was calculated by use of the equation (27)

$$\log p = 9.81137 - \frac{1349}{t^{\circ}\text{C.} + 273.16}$$

The melting point of mercury was taken as -38.87°C. These data were then compared with the so-called "standard" thermocouple. A summary of the calculations are presented in Table 45.

A theoretical consideration of thermocouples has

attained by the subliming carbon dioxide. Observations were taken until a steady value of the thermocouple output was observed. The barometric pressure was read at intervals. The data are presented in Table 42.

The hot junction of the thermocouple was mounted in a test tube containing about 50 cc. of mercury (Rohr and French, triple distilled). The test tube was fitted with an outer jacket, the assembly was immersed in a dry ice-trichloroethylene bath at -50°C . and EMF readings were taken. After the mercury was completely frozen, the cold bath was removed and the assembly was permitted to warm up. During the warming process, EMF readings were taken. These data are presented in Tables 43-44.

The barometric pressure was corrected for temperature effects by use of the equation

$$p = \frac{1 + (1.84 \times 10^{-5})(t - t_0)}{1 + (1.818 \times 10^{-5})(t - t_0)} \times p_0$$

The sublimation temperature of solid carbon dioxide was calculated by use of the equation (27)

$$\log p = 9.81137 - \frac{1349}{t - 273.15}$$

The melting point of mercury was taken as -38.87°C . These data were then compared with the so-called "standard" thermocouples. A summary of the calculations are presented in Table 45.

A theoretical consideration of thermocouples has

shown that for most metals the values of the EMF's plotted against the temperature of the hot junction gives rise to a curve which is sensibly a parabola (7). The equation for this curve is given as

$$E = at + bt^2$$

(see p. 126)

shown that for most metals the values of the EMF's plotted against the temperature of the hot junction give rise to a curve which is sensibly a parabola (7). The equation for this curve is given as

$$E = at + bt^2$$

(see p. 122)

Table 42

Calibration of Thermocouple TC-B at CO₂ Point
March 26, 1948

p = 772.00 mm.
t = 24.0° C.

Zero Time: 11:10 p.m.

Time (min.)	Battery	Rest Point Before	Rest Point After	Potentiometer Setting (μ v)	Galvanometer Reading	Remarks
15	39.5	39.5	39.4	2714	off the scale	Heater current-0.1 amp.
26	39.5	39.4	39.4	2714	off the scale	
33	39.0	39.3	--	2714	off the scale	
37	39.0	39.1	39.1	2714	27.0-drifting	Heater current-0.25 amp
40	39.0	39.7	39.7	2714	29.5	Tightened telescope
				2719	43.4	clamps. Changed
						rest point.
45	39.5	39.7	39.7	2714	29.2	
				2719	43.1	
50	39.5	39.7	39.7	2714	29.2	
				2719	43.1	
55	39.5	39.7	39.7	2714	28.9	
				2719	42.9	
60	39.5	39.5	39.5	2714	28.7	Heater current
				2719	42.7	= 0.1 amp.
65	39.5	39.4	39.4	2714	28.7	- p = 770.80 mm.
				2719	42.6	t = 24.0° C.
70	39.5	39.4	39.4	2714	28.4	
				2719	42.3	
75	39.5	39.4	39.4	2714	28.5	
				2719	42.5	
80	39.5	39.3	39.4	2714	28.2	
				2719	42.2	
85	39.5	39.4	39.3	2714	28.3	
				2719	42.2	
90	39.5	39.3	39.3	2714	28.3	
				2719	42.3	
95	39.5	39.3	39.3	2714	28.3	
				2719	42.3	
100	39.5	39.3	39.3	2714	28.3	p = 770.30 mm.
				2719	42.2	t = 24.1° C.

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Table 43

Calibration of Thermocouple TC-B at Freezing
Point of Mercury

March 20, 1948

Zero Time: 2:25 p.m.

Bath Temperature: -50° C.

Time (min.)	Battery	Rest Point Before	Rest Point After	Potentiometer Setting (mV)	Galvanometer Reading (cm.)
10	31.9	31.8	31.8	1420	18.7
				1425	34.7
12	31.9	31.8	31.8	1420	19.6
				1425	35.6
14	31.9	31.8	31.8	1420	20.1
				1425	36.2
16	31.9	31.8	31.8	1420	20.3
				1425	36.6
18	31.9	31.9	32.0	1420	20.4
				1425	36.4
20	31.9	—	—	1420	—
				1425	—
22	31.9	32.0	32.0	1420	20.7
				1425	36.6
24	31.9	31.9	31.8	1420	20.2
				1425	36.5
26	31.9	31.9	31.9	1420	20.0
				1425	36.4
28	31.9	31.9	31.9	1420	19.8
				1425	36.3
30	31.9	31.9	31.9	1420	19.7
				1425	35.9
32	31.9	31.9	31.9	1420	19.1
				1425	35.5
34	31.9	31.9	31.9	1420	17.2
				1425	34.0
36	31.9	31.9	31.9	1420	14.3
				1425	31.5
38	31.9	31.9	31.9	1420	9.7
				1425	27.4
40	31.9	32.0	32.0	1420	0.7
				1425	19.3

Table 43

Calibration of Thermocouple TC-B at Freezing
Point of Mercury

March 20, 1948

Bath Temperature: -50° C.
Zero time: 8:25 p.m.

Time (min.)	Battery Before	Heat Point After	Potentiometer Setting (mV)	Galvanometer Reading (cm.)
10	31.9	31.8	1420	18.7
12	31.9	31.8	1425	24.7
14	31.9	31.8	1420	19.5
16	31.9	31.8	1425	25.5
18	31.9	31.8	1420	20.1
20	31.9	31.8	1425	26.2
22	31.9	31.8	1420	20.8
24	31.9	31.8	1425	26.8
26	31.9	31.9	1420	20.4
28	31.9	31.9	1425	26.4
30	31.9	31.9	1420	—
32	31.9	31.9	1425	—
34	31.9	31.9	1420	20.7
36	31.9	31.9	1425	26.3
38	31.9	31.9	1420	20.2
40	31.9	31.9	1425	26.5
42	31.9	31.9	1420	20.0
44	31.9	31.9	1425	26.4
46	31.9	31.9	1420	19.8
48	31.9	31.9	1425	26.3
50	31.9	31.9	1420	19.7
52	31.9	31.9	1425	26.9
54	31.9	31.9	1420	19.1
56	31.9	31.9	1425	25.5
58	31.9	31.9	1420	17.3
60	31.9	31.9	1425	24.0
62	31.9	31.9	1420	14.3
64	31.9	31.9	1425	31.5
66	31.9	31.9	1420	8.7
68	31.9	31.9	1425	27.4
70	31.9	32.0	1420	0.7
72	31.9	32.0	1425	19.3

Table 44
Calibration of Thermocouple TC-B at Melting
Point of Mercury

March 20, 1948

Zero Time: 3:13 p.m.

Time (min.)	Battery	Rest Point		Potentiometer Setting	Galvanometer Reading
		Before	After	(μ V)	(cm.)
1	32.1	32.1	32.0	1420 1425	8.5 12-13
3	32.1	32.0	32.0	1420 1425	21.2 37.3
5	32.1	32.0	32.0	1420 1425	21.2 37.5
7	32.1	32.1	32.1	1420 1425	21.0 37.4
9	32.0	32.1	32.0	1420 1425	21.3 37.6
11	32.0	32.0	32.0	1420 1425	21.7 37.6
13	32.0	32.0	32.0	1420 1425	22.5 38.6
15	32.0	32.0	32.0	1420 1425	24.2 40.3
17	32.0	32.0	32.0	1420 1425	25.7 41.6
19	32.0	32.0	32.0	1420 1425	28.6 44.5
21	32.0	32.0	32.0	1420 1425	31.3 46.6
23	32.0	32.0	32.0	1420 1425	37.0 51.3
25	32.0	32.0	—	1420 1425	65-and drifting

Table 44
Calibration of Thermocouple TC-B at Melting
Point of Mercury

March 20, 1948

Zero Time: 3:15 p.m.

Time (min.)	Battery	Rest Point		Setting	Potentialometer Galvanometer Reading
		Before	After		
1	32.1	32.1	32.0	1420	8.5
2	32.1	32.0	32.0	1425	12-15
3	32.1	32.0	32.0	1420	21.2
4	32.1	32.0	32.0	1425	27.3
5	32.1	32.0	32.0	1420	21.2
6	32.1	32.1	32.1	1425	27.5
7	32.1	32.1	32.1	1420	21.0
8	32.0	32.1	32.0	1425	27.4
9	32.0	32.1	32.0	1420	21.3
10	32.0	32.0	32.0	1425	27.6
11	32.0	32.0	32.0	1420	21.7
12	32.0	32.0	32.0	1425	27.6
13	32.0	32.0	32.0	1420	22.2
14	32.0	32.0	32.0	1425	28.3
15	32.0	32.0	32.0	1420	24.3
16	32.0	32.0	32.0	1425	40.3
17	32.0	32.0	32.0	1420	28.7
18	32.0	32.0	32.0	1425	41.3
19	32.0	32.0	32.0	1420	28.6
20	32.0	32.0	32.0	1425	44.3
21	32.0	32.0	32.0	1420	31.3
22	32.0	32.0	32.0	1425	46.3
23	32.0	32.0	32.0	1420	37.0
24	32.0	—	32.0	1425	51.3
25	32.0	—	32.0	1420	55-and drifting

Table 45

Summary of Calculations for Thermocouple TC-B
Calibration

At sublimation temperature of solid carbon dioxide:

Observed pressure	770.55 mm.
Corrected pressure	767.47 mm.
Calculated sublimation temperature	-78.38° C.
Observed EMF	2717.9 μ v.
Standard EMF	2713.7 μ v.
Deviation	4.4 μ v.

At freezing point of mercury:

Freezing point	-38.87° C.
Observed EMF	1423.6 μ v.
Standard EMF	1423.6 μ v.
Deviation	0.0 μ v.

Table 42

Summary of Calculations for Thermocouple TC-2
Calibration

At sublimation temperature of solid carbon dioxide:

Observed pressure	770.55 mm.
Corrected pressure	767.47 mm.
Calculated sublimation temperature	-78.38° C.
Observed EMP	2717.9 mv.
Standard EMP	2713.7 mv.
Deviation	4.2 mv.

At freezing point of mercury:

Freezing point	-38.87° C.
Observed EMP	1423.6 mv.
Standard EMP	1423.6 mv.
Deviation	0.0 mv.

Substituting, in turn, the sublimation temperature of solid carbon dioxide and the melting point of mercury, expressed as degrees centigrade, for t , and the corresponding EMF's in μv for E , the simultaneous equations are obtained

$$2717.9 = -78.38a + (-78.38)^2 b$$

$$1423.6 = -38.87a + (-38.87)^2 b$$

Solving, $a = -38.52$

$$b = -0.04869$$

whence, the equation becomes

$$E = -38.52t - 0.04869t^2$$

Using this equation, a detailed working table of EMF's was calculated for the temperature range involved in the purification procedure (Table 46).

Calibration of Thermocouples TC-C and TC-D.

The thermocouples were mounted in a Claisen flask and distilled water was boiled past the thermocouples. Readings of the output of the thermocouples were taken at regular intervals in the usual way. The data for thermocouple TC-C is presented in Table 47; for thermocouple TC-D in Table 48.

Tin (National Bureau of Standards Sample, m.pt. = 231.9°C.) was melted into a test tube and covered with a layer of paraffin. The thermocouples were mounted in the tin, the test tube was jacketed, and readings were taken on the freezing point. It was found impossible to obtain satisfactory warming curves on the sample with this apparatus because of the difficulty encountered in controlling the heat input,

Substituting, in turn, the sublimation temperature of solid carbon dioxide and the melting point of mercury, expressed as degrees centigrade, for t , and the corresponding EMP's

in q for E , the simultaneous equations are obtained

$$2717.9 = -78.322 + (-78.322) \cdot b$$

$$1432.8 = -38.272 + (-38.272) \cdot b$$

Solving,

$$b = -0.04869$$

whence, the equation becomes

$$E = -38.272 - 0.04869 \cdot b$$

Using this equation, a detailed working table of EMP's was

calculated for the temperature range involved in the purification procedure (Table 48).

Calibration of Thermocouples TC-3 and TC-2.

The thermocouples were mounted in a Claisen flask

and distilled water was boiled past the thermocouples. Readings of the output of the thermocouples were taken at regular

intervals in the usual way. The data for thermocouple TC-3

is presented in Table 47; for thermocouple TC-2 in Table 48.

Tin (National Bureau of Standards Sample, m.p. =

231.9°C.) was melted into a test tube and covered with a

layer of paraffin. The thermocouples were mounted in the tin,

the test tube was jacketed, and readings were taken on the

freezing point. It was found impossible to obtain satisfactory

freezing curves on the sample with this apparatus because

of the difficulty encountered in controlling the heat input,

the source of which was a Bunsen burner. The freezing point data are recorded in Table 49 for thermocouple TC-C; in Table 50 for thermocouple TC-D.

		(°C.)	
-12.00	455.2	-15.25	575.1
-12.25	464.0	-15.50	582.3
-12.50	473.3	-15.75	584.0
-12.75	483.2	-16.00	593.2
-13.00	492.3	-16.25	593.1
-13.25	501.0	-16.50	595.3
-13.50	511.1	-16.75	591.6
-13.75	520.4	-17.00	590.2
-14.00	530.2	-17.25	590.0
-14.25	539.0	-17.50	589.2
-14.50	548.3	-17.75	588.4
-14.75	557.5	-18.00	577.5
-15.00	566.8	-18.25	585.7

the source of which was a Bunsen burner. The freezing point

data are recorded in Table 43 for thermocouple TC-C; in

Table 50 for thermocouple TC-D.

Table 46

Working Table for Thermocouple TC-B in
the Range - 12.000 C. to - 18.250 C.

(°C.)	E _{TC-B}	(°C.)	E _{TC-B}
-12.00	455.2	-15.25	576.1
-12.25	464.6	-15.50	585.3
-12.50	473.9	-15.75	594.6
-12.75	483.2	-16.00	603.8
-13.00	492.5	-16.25	613.1
-13.25	501.8	-16.50	622.3
-13.50	511.1	-16.75	631.5
-13.75	520.4	-17.00	640.8
-14.00	530.0	-17.25	650.0
-14.25	539.0	-17.50	659.2
-14.50	548.3	-17.75	668.4
-14.75	557.6	-18.00	677.5
-15.00	566.8	-18.25	686.7

Table 45

Working Table for Thermocouple TC-B in
the Range - 12.000 C. to - 18.250 C.

TC-B	(°C.)	TC-B	(°C.)
576.1	-12.25	455.2	-12.00
582.3	-12.50	454.8	-12.25
584.6	-12.75	453.9	-12.50
593.8	-13.00	452.2	-12.75
593.1	-13.25	452.8	-13.00
592.2	-13.50	451.8	-13.25
591.5	-13.75	451.1	-13.50
540.8	-14.00	450.4	-13.75
530.0	-14.25	450.0	-14.00
528.2	-14.50	449.0	-14.25
528.4	-14.75	448.2	-14.50
527.2	-15.00	447.2	-14.75
526.7	-15.25	446.8	-15.00

Table 47

Calibration Data for Thermocouple TC-C
at the Boiling Point of Water

June 25, 1948

Zero Time: 2:45 p.m.

Pressure: 767.8 mm.

$t = 24.0^{\circ} \text{C.}$

Time (min.)	Batteries	Rest Point Before	After	Potentiometer Setting	Galvanometer Reading
1	37.0	37.1	37.1	4273 4278	28.8 39.4
6	37.0	37.1	37.1	4273 4278	27.8 38.3
10	37.0	37.1	37.1	4274 4279	29.3 40.0
15	37.0	37.0	37.0	4274 4279	29.3 40.0
20	37.0	37.0	37.0	4274 4279	29.3 40.0
25	37.0	36.9	36.9	4274 4279	29.2 39.8

June 28, 1948

Zero Time: 10:30 p.m.

Pressure: 765.8

$t = 21.0^{\circ} \text{C.}$

3					
3	35.0	34.9	34.9	4271 4276	28.7 39.4
15	35.0	34.7	34.7	4271 4276	29.0 39.9
20	34.5	34.6	34.6	4271 4276	28.8 39.9
30	34.5	34.6	34.6	4271 4276	28.8 39.4
45	34.5	34.6	34.6	4271 4276	28.5 39.2
55	34.5	34.6	34.6	4271 4276	28.1 39.2
60	34.5	34.7	34.7	4271 4276	28.2 39.0
70	34.5	34.7	34.7	4271 4276	28.6 39.3

Table 47

Calibration Data for Thermopile TC-C
at the Boiling Point of Water

June 25, 1948

Zero Time: 2:45 P.M.
Pressure: 757.8 mm.
 $t = 24.0^\circ \text{C.}$

Time (min.)	Batteries	Rest Point Before	Rest Point After	Potentiometer Reading	Potentiometer Galvanometer Reading
1	37.0	37.1	37.1	4275	28.8
5	37.0	37.1	37.1	4278	29.4
10	37.0	37.1	37.1	4275	29.8
15	37.0	37.1	37.1	4278	30.3
20	37.0	37.0	37.0	4275	30.8
25	37.0	37.0	37.0	4278	31.3
30	37.0	37.0	37.0	4275	31.8
35	37.0	37.0	37.0	4278	32.3
40	37.0	37.0	37.0	4275	32.8
45	37.0	37.0	37.0	4278	33.3
50	37.0	37.0	37.0	4275	33.8
55	37.0	37.0	37.0	4278	34.3
60	37.0	37.0	37.0	4275	34.8
65	37.0	37.0	37.0	4278	35.3
70	37.0	37.0	37.0	4275	35.8
75	37.0	37.0	37.0	4278	36.3
80	37.0	37.0	37.0	4275	36.8
85	37.0	37.0	37.0	4278	37.3
90	37.0	37.0	37.0	4275	37.8
95	37.0	37.0	37.0	4278	38.3
100	37.0	37.0	37.0	4275	38.8

June 26, 1948

Zero Time: 10:30 P.M.
Pressure: 755.8
 $t = 21.0^\circ \text{C.}$

3	35.0	34.9	34.9	4271	28.7
5	35.0	34.9	34.9	4275	29.1
10	35.0	34.9	34.9	4271	29.0
15	35.0	34.9	34.9	4275	29.8
20	34.8	34.8	34.8	4271	30.8
25	34.8	34.8	34.8	4275	30.9
30	34.8	34.8	34.8	4271	31.3
35	34.8	34.8	34.8	4275	31.4
40	34.8	34.8	34.8	4271	31.8
45	34.8	34.8	34.8	4275	32.3
50	34.8	34.8	34.8	4271	32.8
55	34.8	34.8	34.8	4275	33.1
60	34.8	34.7	34.7	4271	33.3
65	34.8	34.7	34.7	4275	33.8
70	34.8	34.7	34.7	4271	34.0
75	34.8	34.7	34.7	4275	34.3
80	34.8	34.7	34.7	4271	34.8
85	34.8	34.7	34.7	4275	35.3
90	34.8	34.7	34.7	4271	35.8
95	34.8	34.7	34.7	4275	36.3
100	34.8	34.7	34.7	4271	36.8

Table 48

Calibration Data for Thermocouple TC-D
at the Boiling Point of Water

August 30, 1948

Zero Time: 12:30 p.m.

Pressure: 762.7 mm.

$t = 26.8^{\circ} \text{C.}$

Time (min.)	Batteries	Rest Point Before	Rest Point After	Potentiometer Setting	Galvanometer Reading
1	34.0	34.1	34.1	---	---
5	34.0	33.8	33.8	---	---
10	34.0	33.8	33.8	4265	26.7
				4270	35.3
15	34.0	31.7	31.6	4267	22.3
				4272	32.1
25	34.0	31.5	31.3	4270	28.0
				4275	36.4
30	31.0	31.3	31.3	4270	28.2
				4275	38.0
35	31.0	31.1	31.1	4270	28.1
				4275	37.8
40	31.0	30.9	30.9	4270	27.8
				4275	37.7
50	31.0	30.7	30.7	4270	27.7
				4275	37.5

Table 48

Calibration Data for Thermocouple TC-D
at the Boiling Point of Water

August 30, 1948

Zero Time: 12:30 p.m.
Pressure: 782.7 mm.
t = 28.8° C.

Time (min.)	Batteries	Rest Point Before After	Potentiometer Setting	Potentiometer Galvanometer Reading
1	34.0	34.1 34.1	4275	38.7
5	34.0	33.8 33.8	4275	38.3
10	34.0	33.8 33.8	4275	38.3
15	34.0	31.7 31.8	4275	38.1
20	34.0	31.5 31.8	4275	38.0
25	31.0	31.3 31.3	4275	38.0
30	31.0	31.1 31.1	4275	37.8
35	31.0	30.9 30.9	4275	37.8
40	31.0	30.7 30.7	4275	37.8
45	31.0	30.7 30.7	4275	37.8

Table 49

Calibration Data for Thermocouple TC-C
at the Melting Point of Tin

July 24, 1948

Run 1

Time (min.)	Batteries	Rest Point Before	Rest Point After	Potentiometer Setting	Galvanometer Reading
1	36.5	36.5	36.5	13845	36.5
2	36.5	36.5	36.5	13000	36.5
3	36.5	36.5	36.5	12247	36.5
4	36.5	36.5	36.5	11615	36.5
5	36.5	36.5	36.5	11100	36.5
6	36.5	36.5	36.5	10595	36.5
7	36.5	36.3	36.3	10975	30.7
				10980	37.4
10	36.5	36.3	36.3	10975	30.1
				10980	37.1
13	36.5	36.3	36.3	10975	31.7
				10980	40.5
15	36.5	36.3	36.3	10975	drifting
				10980	

Run 2

1	33.0	33.0	33.0	12360	33.0
2	33.0	33.0	33.0	11618	33.0
3	33.0	33.0	33.0	11049	33.0
4	33.0	33.0	33.0	10486	33.0
5	33.0	33.0	33.0	10980	32.3
				10985	39.3
6	33.0	33.0	33.0	10980	32.5
				10985	39.4
7	33.0	33.0	33.0	10980	32.4
				10985	39.2
8	33.0	32.9	32.9	10980	32.3
				10985	39.2
9	33.0	32.9	32.9	10980	32.3
				10985	39.3
10	33.0	32.8	--	10980	drifting

Table 49

Calibration Data for Thermocouple TC-2
at the Melting Point of Tin

July 24, 1948

Run 1

Time (min.)	Batteries	Heat Point Before	Heat Point After	Potentiometer Setting	Galvanometer Reading
1	38.5	38.5	38.5	10845	38.5
2	38.5	38.5	38.5	10800	38.5
3	38.5	38.5	38.5	10847	38.5
4	38.5	38.5	38.5	11815	38.5
5	38.5	38.5	38.5	11100	38.5
6	38.5	38.5	38.5	10835	38.5
7	38.5	38.5	38.5	10875	30.7
				10880	37.4
10	38.5	38.5	38.5	10875	30.1
				10880	37.1
15	38.5	38.5	38.5	10875	31.7
				10880	40.5
18	38.5	38.5	38.5	10875	drifting
				10880	

Run 2

1	33.0	33.0	33.0	10360	33.0
2	33.0	33.0	33.0	11818	33.0
3	33.0	33.0	33.0	11045	33.0
4	33.0	33.0	33.0	10485	33.0
5	33.0	33.0	33.0	10880	33.3
				10885	30.3
6	33.0	33.0	33.0	10880	33.5
				10885	30.4
7	33.0	33.0	33.0	10880	32.4
				10885	30.2
8	33.0	33.0	33.0	10880	32.3
				10885	30.2
9	33.0	33.0	33.0	10880	32.3
				10885	32.3
10	33.0	33.0	33.0	10880	drifting

Table 49
(concluded)

Run 3

Time (min.)	Batteries	Rest Point Before	Point After	Potentiometer Setting	Galvanometer Reading
1	33.0	33.0	33.0	13384	33.0
2	33.0	33.0	33.0	12786	33.0
3	33.0	33.0	33.0	12170	33.0
4	33.0	33.0	33.0	11552	33.0
5	33.0	33.0	33.0	10940	33.0
6	33.0	33.0	33.0	10420	33.0
7	33.0	32.9	33.3	10980	33.7
				10985	40.7
9	33.0	33.3	33.3	10980	33.3
				10985	40.2
11	33.0	33.3	33.3	10980	33.3
				10985	40.2
13	33.0	33.3	33.0	10980	33.2
				10985	40.2

Table 49
(continued)

Run 3

Time (min.)	Batteries	Rest Point Before	Rest Point After	Potentiometer Setting	Potentiometer Galvanometer Reading
1	33.0	33.0	33.0	13384	33.0
2	33.0	33.0	33.0	12785	33.0
3	33.0	33.0	33.0	12170	33.0
4	33.0	33.0	33.0	11552	33.0
5	33.0	33.0	33.0	10940	33.0
6	33.0	33.0	33.0	10420	33.0
7	33.0	33.0	33.3	10920	33.7
				10985	40.7
8	33.0	33.3	33.3	10980	33.3
				10985	40.2
11	33.0	33.3	33.3	10980	33.3
				10985	40.2
13	33.0	33.3	33.0	10980	33.2
				10985	40.2

Table 50

Calibration Data for Thermocouple TC-D
at the Melting Point of Tin

(12 Runs were Done on TC-D. The three closest to
the average of the 12 are here presented.)

Time (min.)	Batteries	Rest Point Before	Rest Point After	Potentiometer Setting	Galvanometer Reading
July 27, 1948					
Run 4					
1	31.0	31.6	31.6	12971	31.6
2	31.5	31.6	31.6	12000	31.6
3	31.5	31.6	31.6	11420	31.6
4	31.5	31.5	31.5	10790	31.5
5	31.5	31.5	31.5	10971	23.5
				10976	29.7
9	31.5	31.5	31.3	10971	23.3
				10976	29.5
11	31.5	31.3	—	10971	23.8
				10976	drifting
July 29, 1948					
Run 10					
5	28.5	28.7	28.7	10976	26.3
				10981	32.6
7	28.5	28.7	28.7	10976	26.3
				10981	32.6
9	28.5	28.7	—	10976	26.8
				10981	drifting
July 29, 1948					
Run 12					
3½	28.5	—	—	10976	—
5	28.5	—	—	10976	—
6	28.5	28.5	28.5	10976	27.7
				10981	33.9
7½	28.5	28.5	28.5	10976	26.8
				10981	33.3
9	28.5	28.5	28.5	10976	26.8
				10981	33.4
10½	28.5	28.5	28.5	10976	26.7
				10981	33.2
12	28.5	28.5	28.5	10976	drifting

Table 50

Calibration Data for Thermocouple TC-D
at the Melting Point of Tin

(12 Runs were done on TC-D. The three closest to
the average of the 12 are here presented.)

Time (min.) Batteries Before After Rest Point Potentiometer Galvanometer Reading

July 27, 1948

Run 4				
1	31.0	31.5	31.5	31.5
2	31.5	31.5	31.5	31.5
3	31.5	31.5	31.5	31.5
4	31.5	31.5	31.5	31.5
5	31.5	31.5	31.5	31.5
6	31.5	31.5	31.5	31.5
7	31.5	31.5	31.5	31.5
8	31.5	31.5	31.5	31.5
9	31.5	31.5	31.5	31.5
10	31.5	31.5	31.5	31.5
11	31.5	31.5	31.5	31.5
12	31.5	31.5	31.5	31.5

July 29, 1948

Run 10				
5	28.5	28.7	28.7	28.7
6	28.5	28.7	28.7	28.7
7	28.5	28.7	28.7	28.7
8	28.5	28.7	28.7	28.7
9	28.5	28.7	28.7	28.7
10	28.5	28.7	28.7	28.7
11	28.5	28.7	28.7	28.7
12	28.5	28.7	28.7	28.7

July 29, 1948

Run 12				
3	28.5	28.5	28.5	28.5
4	28.5	28.5	28.5	28.5
5	28.5	28.5	28.5	28.5
6	28.5	28.5	28.5	28.5
7	28.5	28.5	28.5	28.5
8	28.5	28.5	28.5	28.5
9	28.5	28.5	28.5	28.5
10	28.5	28.5	28.5	28.5
11	28.5	28.5	28.5	28.5
12	28.5	28.5	28.5	28.5

The EMF's corresponding to the steam point and the melting point of tin were calculated and these results are listed in Table 51, along with the EMF values, corresponding to the temperatures at which the experimental readings were taken, of a standard thermocouple (12) (Table 52).

With these data it was ~~was~~ possible to plot deviation functions for thermocouples TC-C (Figure 23) and TC-D (Figure 24).

An example will best illustrate the use of these calibration graphs. Consider Point 4 of Run 3, that portion, in particular, which relates to Thermostat "A" (whose temperature was measured by TC-C). In the reading taken at 4 hrs. 30 min., the data are

4127	37.5
4132	49.9

The rest point is 38.7 Therefore the output of the thermocouple at this temperature is

$$4127 + \frac{(38.7-37.5)(5)}{49.9-37.5} = 4127.5 \text{ uv.}$$

Using Figure 23, we find that at 4127.5 uv, the deviation from the standard thermocouple is 11.2 uv., that is, if 11.2 uv. are added to the observed reading, one obtains the reading which would be observed with the standard thermocouple. Then, using Table 52, interpolation is made and the temperature is found to be 97.08° C.

The EMF's corresponding to the steam point and the melting point of tin were calculated and these results are listed in Table 31, along with the EMF values, corresponding to the temperatures at which the experimental readings were taken, of a standard thermocouple (12) (Table 32).

With these data it was impossible to plot deviation functions for thermocouples TC-C (Figure 33) and TC-D (Figure 34).

An example will best illustrate the use of these calibration graphs. Consider Point 4 of Run 3, first portion, in particular, which relates to Thermostat "A" (whose temperature was measured by TC-C). In the reading taken at 4 hrs. 30 min., the data are

4127	37.5
4132	49.9

The rest point is 38.7. Therefore the output of the thermocouple at this temperature is

$$4127 + \frac{(38.7-37.5)(5)}{49.9-37.5} = 4127.5 \text{ mv.}$$

Using Figure 33, we find that at 4127.5 mv, the deviation from the standard thermocouple is 11.2 mv., that is, 11.2 mv. are added to the observed reading, one obtains the reading which would be observed with the standard thermocouple. Then, using Table 32, interpolation is made and the temperature is found to be 97.08° C.

Table 51

Summary of the Calibration Data of Thermocouple
TC-C and TC-D at the Boiling Point of
Water and the Melting Point of Tin

Thermocouple TC-C

At the steam point:

Run 1 Observed EMF at 100.29° C. 4277.6 μ v.

Calculated EMF at 100.29° C. 4289.3 μ v.

(from Standard Thermocouple)

Deviation 11.7 μ v.

Run 2 Observed EMF at 100.20° C. 4273.8 μ v.

Calculated EMF at 100.20° C. 4285.3 μ v.

(from Standard Thermocouple)

Deviation 11.5 μ v.

At the melting point of tin:

Observed EMF (Run 1) 10979.4 μ v.

" " (Run 2) 10980.5 μ v.

" " (Run 3) 10980.0 μ v.

Calculated EMF at 231.9° C. 11008.8 μ v.

(from Standard Thermocouple)

Deviation 28.8 μ v.

Table 51

Summary of the Calibration Data of Thermocouples
TC-3 and TC-5 at the Boiling Point of
Water and the Melting Point of Tin

Thermocouple TC-3

At the steam point:

Run 1	Observed EMF at 100.25° C.	4277.8 mv.
	Calculated EMF at 100.25° C.	4282.3 mv.
(from Standard Thermocouples)		
	Deviation	11.7 mv.

Run 2	Observed EMF at 100.25° C.	4275.8 mv.
	Calculated EMF at 100.25° C.	4282.3 mv.
(from Standard Thermocouples)		
	Deviation	11.5 mv.

At the melting point of tin:

Observed EMF (Run 1)	10375.4 mv.
" (Run 2)	10380.5 mv.
" (Run 3)	10380.0 mv.
Calculated EMF at 231.9° C.	11002.8 mv.
(from Standard Thermocouples)	
Deviation	28.8 mv.

Table 51
(concluded)

Thermocouple TC-D

At the steam point:

Observed EMF at 100.10° C. 4271.6 μ v.

Calculated EMF at 100.10° C. 4280.4 μ v.

(from Standard Thermocouple)

Deviation 8.8 μ v.

At the melting point of tin:

Observed EMF (Run 1) 10974.3 μ v.

" " (Run 2) 10973.6 μ v.

" " (Run 3) 10976.2 μ v.

" " (Run 4) 10977.5 μ v.

" " (Run 5) 10979.1 μ v.

" " (Run 6) 10979.2 μ v.

" " (Run 7) 10978.9 μ v.

" " (Run 8) 10980.3 μ v.

" " (Run 9) 10980.0 μ v.

" " (Run 10) 10977.9 μ v.

" " (Run 11) 10978.6 μ v.

" " (Run 12) 10977.3 μ v.

Average 10977.7 μ v.

Calculated EMF at 231.9° C. 11008.8 μ v.

(from Standard Thermocouple)

Deviation 31.1 μ v.

Table 51
(continued)

Thermocouple TC-D

At the steam point:

Observed EMT at 100.10° C. 4271.6 mv.
Calculated EMT at 100.10° C. 4280.4 mv.

(from Standard Thermocouple)

Deviation 8.8 mv.

At the melting point of tin:

Observed EMT	(Run 1)	10274.3 mv.
"	(Run 2)	10272.6 mv.
"	(Run 3)	10276.2 mv.
"	(Run 4)	10277.5 mv.
"	(Run 5)	10279.1 mv.
"	(Run 6)	10278.2 mv.
"	(Run 7)	10276.9 mv.
"	(Run 8)	10280.3 mv.
"	(Run 9)	10280.0 mv.
"	(Run 10)	10277.9 mv.
"	(Run 11)	10278.6 mv.
"	(Run 12)	10277.3 mv.

Average

Calculated EMT at 231.9° C. 11008.8 mv.

(from Standard Thermocouple)

Deviation 31.1 mv.

Table 52

EMF - Temperature Relationship
of Standard Thermocouple

(International Critical Tables, 1 , 58)

E (μ v.)	0	1000	2000	3000	4000	5000	6000
0	0	25.27	49.20	72.08	94.07	115.31	135.91
100	2.59	27.72	51.53	74.31	96.23	117.40	137.94
200	5.16	30.15	53.85	76.54	98.38	119.48	139.96
300	7.72	32.57	56.16	78.76	100.52	121.56	141.98
400	10.27	34.98	58.46	80.97	102.66	123.63	143.99
500	12.80	37.38	60.76	83.17	104.79	125.69	146.00
600	15.32	39.77	63.04	85.37	106.91	127.75	148.00
700	17.83	42.15	65.31	87.56	109.02	129.80	150.00
800	20.32	44.51	67.58	89.74	111.12	131.84	151.99
900	22.80	46.86	69.83	91.91	113.22	133.88	153.97
1000	25.27	49.20	72.08	94.07	115.31	135.91	155.95

Table 52
 NTP - Temperature Relationship
 at Standard Atmospheric
 (International Critical Tables, 4, 52)

t (°C.)	0	100	200	300	400	500	600	700	800	900	1000
0	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
100	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
200	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
300	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
400	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
500	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
600	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
700	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
800	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
900	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66
1000	25.27	27.72	29.77	31.24	32.46	33.46	34.26	34.85	35.23	35.50	35.66

Table 52
(concluded)

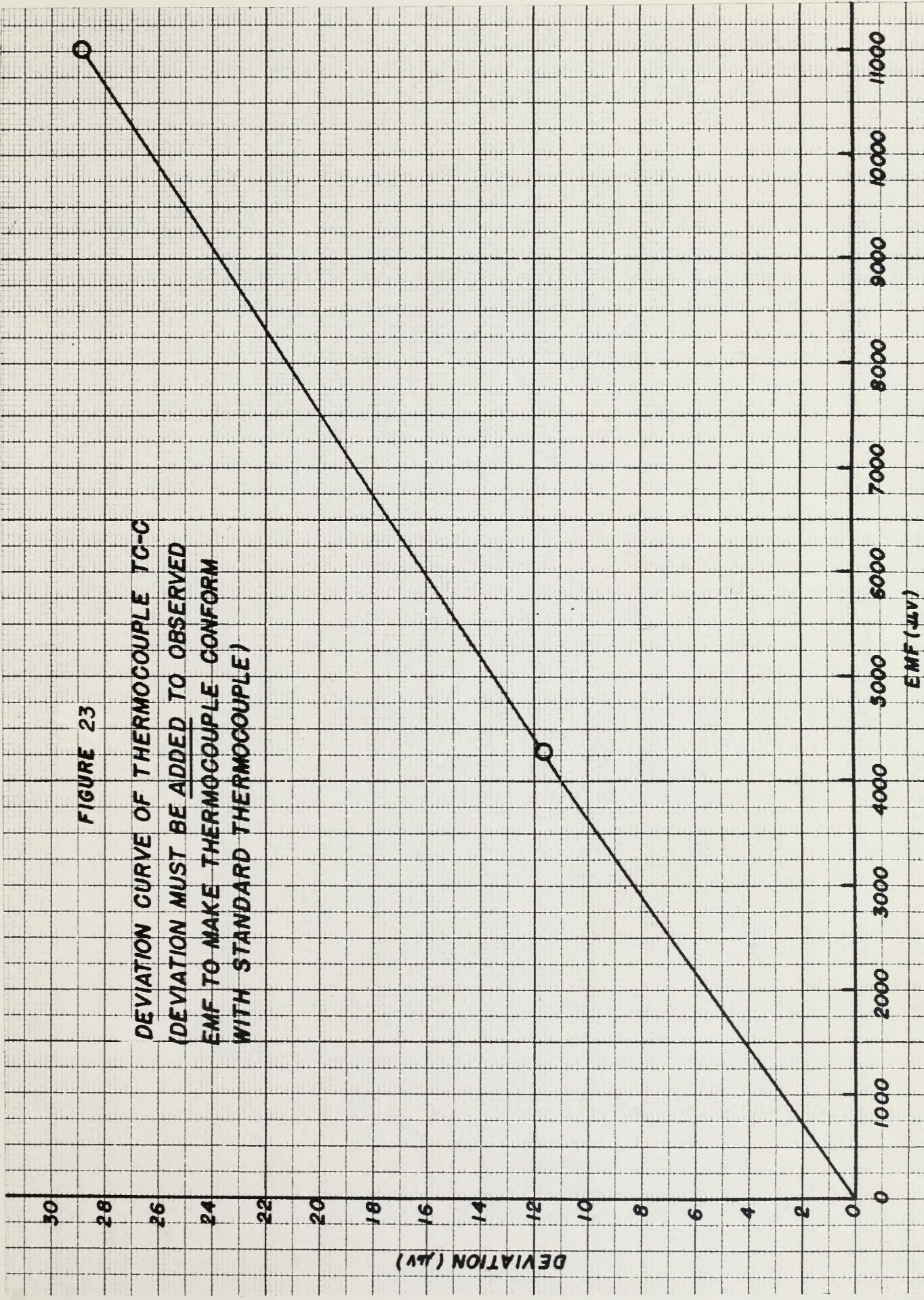
E ($\mu\text{v.}$)	7000	8000	9000	10000	11000	12000
0	155.95	175.50	194.62	213.36	231.74	249.82
100	157.92	177.43	196.51	215.21	233.56	251.61
200	159.89	179.36	198.40	217.06	235.38	253.40
300	161.86	181.28	200.28	218.91	237.20	255.18
400	163.82	183.20	202.16	220.75	239.01	256.96
500	165.78	185.11	204.04	222.59	240.82	258.74
600	167.73	187.02	205.91	224.43	242.63	260.52
700	169.68	188.93	207.78	226.26	244.43	262.29
800	171.62	190.83	209.64	228.09	246.23	264.06
900	173.56	192.73	211.50	229.92	248.03	265.83
1000	175.50	194.62	213.36	231.74	249.82	267.60

Table 53
(continued)

F	7000	8000	9000	10000	11000	12000
0	155.98	155.50	154.82	153.95	152.74	151.23
100	157.92	157.45	156.57	155.51	154.20	152.61
200	159.86	159.38	158.40	157.25	155.84	154.25
300	161.80	161.32	160.34	159.19	157.68	156.09
400	163.74	163.26	162.28	161.13	159.62	158.03
500	165.68	165.20	164.22	163.07	161.56	160.07
600	167.62	167.14	166.16	165.01	163.50	162.01
700	169.56	169.08	168.10	166.95	165.44	163.95
800	171.50	171.02	170.04	168.89	167.38	165.89
900	173.44	172.96	171.98	170.83	169.32	167.83
1000	175.38	174.90	173.92	172.77	171.26	169.77

FIGURE 23

DEVIATION CURVE OF THERMOCOUPLE TC-C
(DEVIATION MUST BE ADDED TO OBSERVED
EMF TO MAKE THERMOCOUPLE CONFORM
WITH STANDARD THERMOCOUPLE)



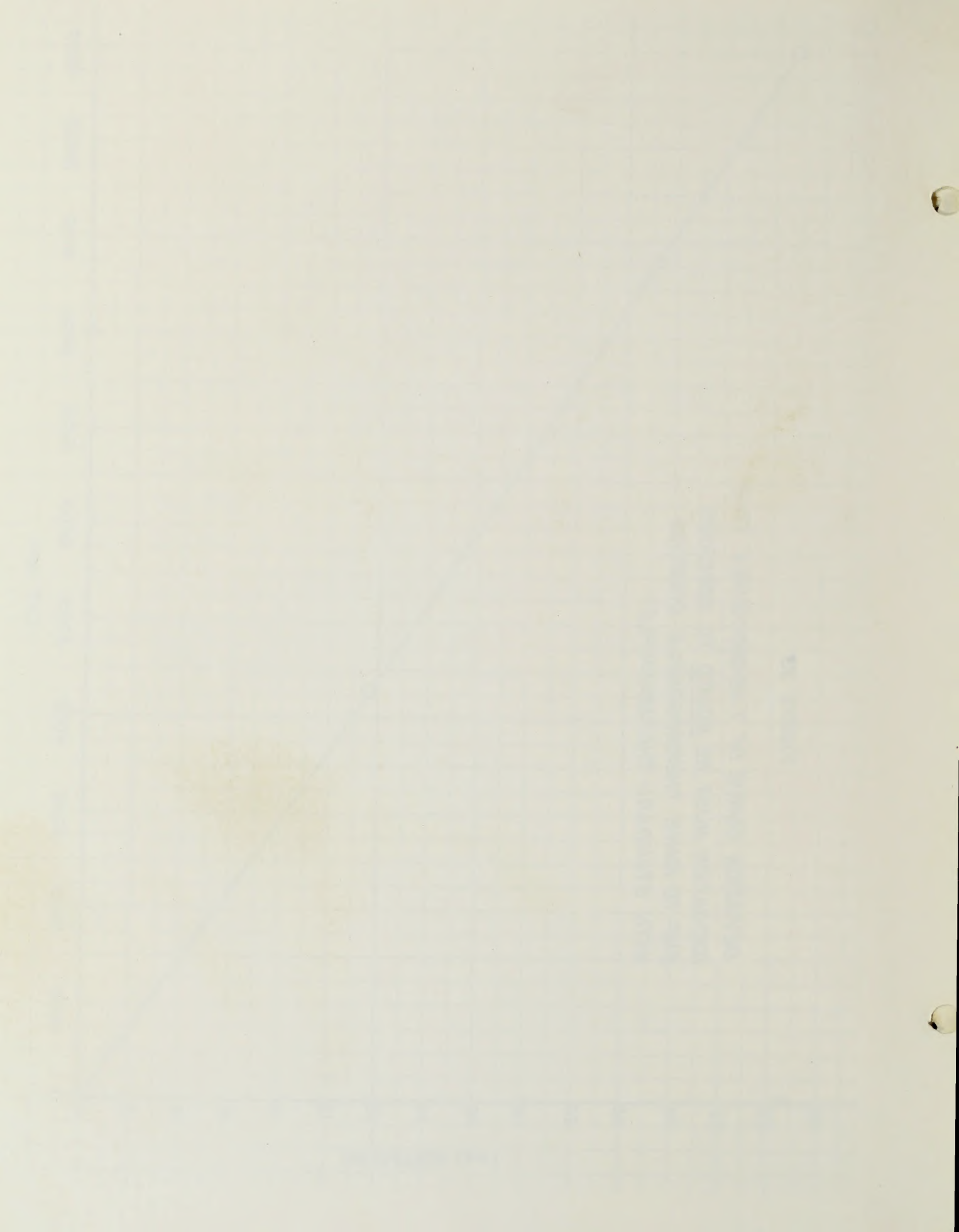
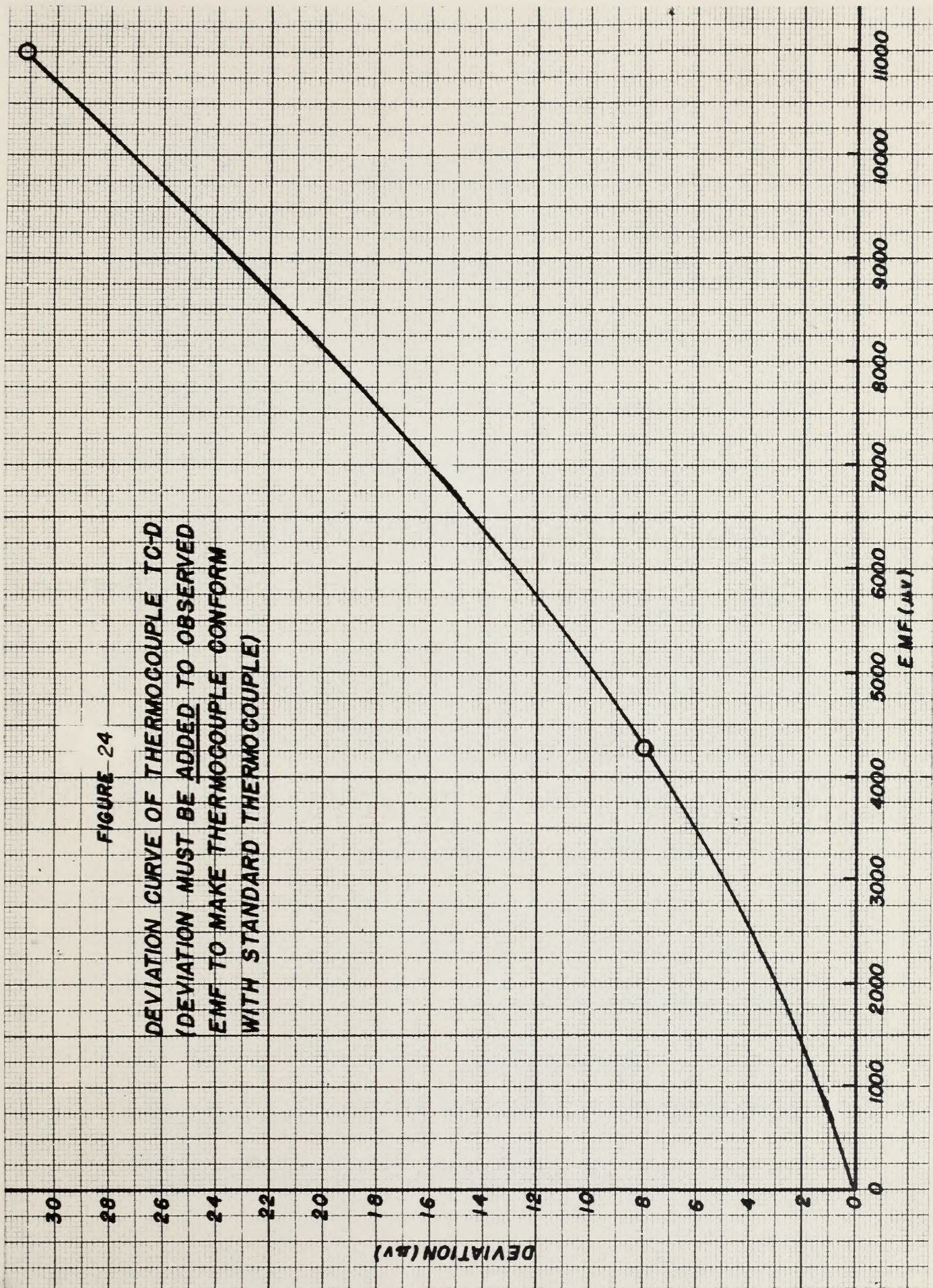


FIGURE 24

DEVIATION CURVE OF THERMOCOUPLE TC-D
(DEVIATION MUST BE ADDED TO OBSERVED
EMF TO MAKE THERMOCOUPLE CONFORM
WITH STANDARD THERMOCOUPLE)



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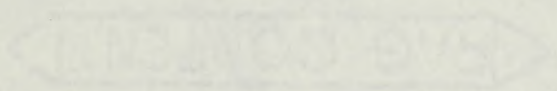
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